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**INTRODUCTION TO  
SEMIMICRO  
QUALITATIVE ANALYSIS**

PRENTICE-HALL CHEMISTRY SERIES  
WENDELL M. LATIMER, *Editor*

# **INTRODUCTION TO SEMIMICRO QUALITATIVE ANALYSIS**

by

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New York  
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1949

INTRODUCTION TO SEMIMICRO QUALITATIVE ANALYSIS.  
*Formerly* INTRODUCTION TO QUALITATIVE ANALYSIS.

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## Preface

This manual has been written for the use of students who wish to take a one-semester course in qualitative analysis and who have a background of one semester of general chemistry. Although designed particularly for use in a sequence where qualitative analysis serves as the laboratory work for the second semester of general chemistry, the book can also be used when qualitative analysis falls in the third quarter or third semester of a sequence in which general chemistry, with conventional laboratory work, occupies the first two quarters or semesters.

As the title suggests, this manual comprises an introduction to qualitative analysis and does not attempt a complete presentation of the subject. However, experience over a period of twelve years has demonstrated that a student who has mastered this introduction is well equipped to go into those advanced courses requiring an understanding of, and a familiarity with, the principles and techniques of qualitative analysis.

Only 21 metals and 13 acids are considered. Furthermore, only those aspects of the chemistry of the cations and anions which have direct bearing on the behavior of these cations and anions in the course of their separation and identification are presented. As a consequence, the content of the manual can be completed in one semester.

Detailed discussions and explanations are presented largely in the form of notes, which are given directly after the procedure or procedures in which they are applied. With this arrangement, the student gets the explanation of an experimental behavior when that behavior is noted.

The author wishes to express his indebtedness to *An Introduction to Qualitative Analysis*, by Sorum and Walton, which is the macro counterpart of this book. He wishes, also, to

express his appreciation for the help that he has received from all members of the General Chemistry Staff at the University of Wisconsin, particularly from G. A. Hall, M. L. Holt, E. M. Larsen, and H. L. Ritter.

C. H. SORUM

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## Note to Instructors

A group of questions will be found at the end of each chapter. These can be used as the basis for an oral review of each chapter's content or they can be assigned as homework. Only a few mathematical problems are included; if the detailed aspects of the solubility product principle are to be covered, the author's *Problems for General Chemistry and Qualitative Analysis* or some comparable problem book should be used as a companion text.

The experimental procedures and specific tests have been checked and rechecked; if the directions are followed with reasonable care, good results will be obtained. Emphasis should be made that the entire success of the copper-arsenic group analysis depends on having good-quality ammonium polysulfide. It is easy to prepare and will keep almost indefinitely if stored in small, well-stoppered bottles. The difficulty involved in using ammonium polysulfide results from the fact that when it is exposed to air, as when placed in desk reagent bottles, it slowly decomposes. This decomposition is easily detected by the deposition of sulfur, whereupon the reagent should immediately be replaced.

Every instructor faces the problem of how best to present equations for reactions that take place. Since those in qualitative analysis are largely ionic, one might well argue that ionic equations should be used. However, there are many reactions where there is honest difference of opinion as to the ionic mechanism. There is also the fact that, since qualitative analysis is concerned with a series of laboratory procedures in which specific reagents are used, the equations should indicate what these specific reagents are. To suit these various situations and points of view, some of the equations are presented ionically, most molecularly, and some in both ways. The

molecular equations are presented with the understanding that, when a student knows the nature of the reactant or product (whether or not it is soluble and whether or not it is a strong electrolyte), he can easily work out the ionic counterpart. In this way the teacher will be allowed latitude in the interpretation of reactions.

C. H. S.

# Contents

CHAPTER	PAGE
1. THE PRACTICE OF QUALITATIVE ANALYSIS . . . . .	1
2. SOLUTIONS AND SOLUBILITY . . . . .	10
3. THE SILVER GROUP . . . . .	36
4. THE COPPER-ARSENIC GROUP . . . . .	53
5. THE ALUMINUM-NICKEL GROUP . . . . .	87
6. THE BARIUM-MAGNESIUM GROUP . . . . .	113
7. THE ANALYSIS OF ALLOYS . . . . .	125
8. PRELIMINARY TESTS FOR ANIONS . . . . .	134
9. SPECIFIC TESTS FOR ANIONS . . . . .	149
10. THE ANALYSIS OF SALTS AND SALT MIXTURES . . . . .	164
11. RECORDING AND REPORTING ANALYSES . . . . .	180
APPENDIX . . . . .	189
INDEX . . . . .	195



**INTRODUCTION TO  
SEMIMICRO  
QUALITATIVE ANALYSIS**





## CHAPTER 1

### The Practice of Qualitative Analysis

THE FIRST SEMESTER's laboratory work in general chemistry was concerned, to a large extent, with the preparation and properties of certain elements and their compounds. In the course of this laboratory work, the student was called upon frequently to *test* for a substance or to prove the *identity* of a substance. Oxygen was *identified* by the fact that it caused a glowing splint to burst into flame, and hydrogen chloride gas was easily recognized by the fact that it fumed strongly in moist air. Carbon dioxide produced a white precipitate of calcium carbonate when passed into limewater, whereas solutions containing sulfate ions gave a white precipitate when treated with a solution of barium ions. Further examples might be cited, all pointing to the fact that a person who has had an introductory laboratory course in general chemistry has learned to *identify* various substances.

In the laboratory work with which this book is concerned, identification of substances will be of primary interest. The study of qualitative analysis is a study of the ways and means by which substances may be identified. Specifically, inorganic qualitative analysis is concerned with finding out which metallic ions (cations) and acid radicals (anions) are present in substances and mixtures of substances.

A complete system of qualitative inorganic analysis would include methods for detecting all metallic ions and all acid radicals as well as all the elements. Not only would procedures be given for the detection of such common metals as copper, tin, iron, aluminum, and zinc and such acid radicals as sulfates, phosphates, and carbonates, but the detection of the less common metals such as rhenium, columbium, platinum, and cerium and such acid radicals as tellurates, molybdates,

ferrocyanides, and vanadates would also be included. Such a complete course would be too involved and difficult for the beginning student of qualitative analysis.

An understanding of the methods of qualitative analysis and a knowledge of the principles which underlie it can be obtained by a study of the identification of a few common and representative metallic ions and acid radicals. Those considered in this course are the following:

*Metallic ions (cations):*  $\text{Ag}^+$ ,  $\text{Pb}^{++}$ ,  $\text{Hg}_2^{++}$ ,  $\text{Hg}^{++}$ ,  $\text{Bi}^{+++}$ ,  $\text{Cu}^{++}$ ,  $\text{Cd}^{++}$ ,  $\text{Sn}^{++}$ ,  $\text{Sn}^{++++}$ ,  $\text{Sb}^{+++}$ ,  $\text{As}^{+++}$ ,  $\text{Fe}^{++}$ ,  $\text{Fe}^{+++}$ ,  $\text{Al}^{+++}$ ,  $\text{Cr}^{+++}$ ,  $\text{Mn}^{++}$ ,  $\text{Zn}^{++}$ ,  $\text{Ni}^{++}$ ,  $\text{Co}^{++}$ ,  $\text{Ba}^{++}$ ,  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ .

*Acid radicals (anions):*  $\text{SO}_4^{--}$ ,  $\text{SO}_3^{--}$ ,  $\text{CO}_3^{--}$ ,  $\text{BO}_3^{--}$ ,  $\text{CrO}_4^{--}$ ,  $\text{PO}_4^{--}$ ,  $\text{AsO}_4^{--}$ ,  $\text{S}^{--}$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{NO}_3^-$ ,  $\text{C}_2\text{H}_3\text{O}_2^-$ .

In order to show how qualitative analysis works out in actual practice, let us take a solution containing all the cations listed above and examine the method by which the presence of each cation is proved.

A first thought might be to add some superreagent which would give a different and very characteristic precipitate with each cation in the mixture. Obviously, however, such a procedure would be no good because the mixture of cations, each giving a different and characteristic precipitate, would give a completely confusing mixture of precipitates.

The answer to this objection would be to find a specific reagent for each cation, a reagent that would give a precipitate or colored solution with one, and only one, cation. If there were such a complete set of specific reagents, qualitative analysis would be very simple. Unfortunately, such an ideal collection of reagents does not exist. With one or two exceptions, a reagent that gives a characteristic reaction with one ion either gives a characteristic reaction with other ions as well or else its characteristic reaction with one ion is interfered with by other ions. In other words, in order to identify a certain cation it must be alone, free from other cations.

The answer to the question of how to proceed with the detection of the cations in the above solution is thus quite obvious. The cations are first *separated*; then they are *identified*. The whole plan of qualitative analysis is a series of *separations* and *identifications*.

The next question is how to go about separating all of the cations listed when they are found together in the same solution. It is possible that a system could be worked out whereby the cations could be separated and identified one at a time. The more practical method, employed in all systems of qualitative analysis, is to separate the cations a handful at a time. The procedure, in brief, is as follows: A small handful of cations, three to be specific, is first taken out. This little handful of three is separated by taking out one and leaving two and then separating these two from each other. The separated cations are then easily identified by means of characteristic reactions.

Having taken out and separated the first handful, we take out a second handful, then a third, leaving a fourth and last handful. The original mixture of cations is separated into four handfuls. Each of these handfuls is separated in turn, and the separated cations are identified. If the handful is a small one, consisting of only three cations, it is separated by taking out one, leaving two and then separating these two. If the handful is a large one, as is actually the case with the second, third, and fourth handfuls, the large handful is first separated into two small handfuls; then the separation proceeds by taking out first one and then another until each cation has been isolated.

The next question is, How do we go about picking out these handfuls? The handfuls, more correctly referred to as *groups*, are taken out by the addition of a specific reagent, called a *group reagent*. This reagent forms insoluble compounds with the cations in that particular group but permits all other cations to remain in solution. The group is thereby **taken out** as a mixture of insoluble substances.

Outline 1 shows the content of each group and the group reagent that is added to precipitate out each group. This outline should be examined carefully, since it gives the whole plan of group separation of cations.

HCl is the group reagent for the first group, called the *silver group*. The separation of the cations of the silver group from all other cations depends on the experimental fact that the chlorides of silver, lead, and mercury I are insoluble in dilute HCl, whereas the chlorides of all other metals are soluble.

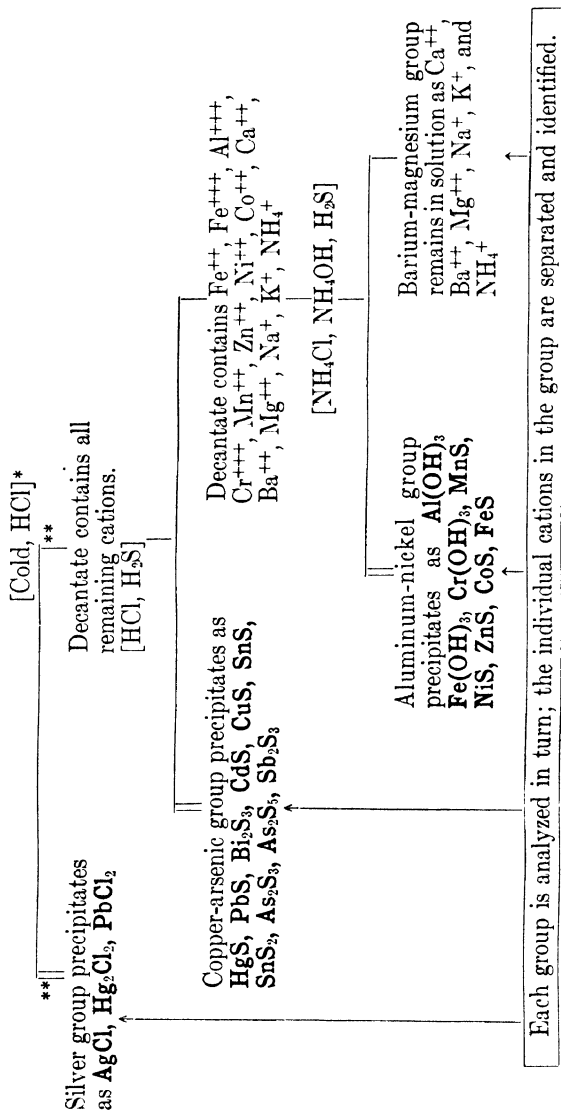
The group reagent for the second group, the copper-arsenic group, is  $\text{H}_2\text{S}$ . The separation of the cations of the copper-arsenic group from the remaining cations depends on the fact that the sulfides of the former are insoluble in HCl, whereas the sulfides of the latter are soluble.

The group reagents for the third group, the aluminum-nickel group, are  $\text{NH}_4\text{OH}$  and  $\text{H}_2\text{S}$ . The sulfides and hydroxides of the cations of the aluminum-nickel group are insoluble in alkaline solution, whereas the sulfides of the cations of the last group, the barium-magnesium group, are soluble.

The last question is, how do we go about separating and identifying the cations in each handful? The detailed answers to that question will be left to Chapters 3, 4, 5, and 6. At this point it will be sufficient to call attention to Outlines 2, 3, 4 and 5, on pages 36, 52, 86, and 112, respectively. These outlines show, schematically, how the separation and identification of the cations in each group are carried out.

It is obvious, from what has been said, that the separation and identification of the cations follows a very orderly plan. It is also obvious, from an examination of Outlines 2, 3, 4, and 5, that the execution of this orderly plan of separation and identification is going to call for careful and extensive laboratory work, and the understanding of the plan is going to require knowledge of a great many principles and facts. So that the student may have a better chance to learn these principles and facts, so that he may acquire the techniques required for the various procedures and may learn to recognize

Solution contains  $\text{Ag}^+$ ,  $\text{Hg}_2^{++}$ ,  $\text{Pb}^{++}$ ,  $\text{Hg}^{++}$ ,  $\text{Bi}^{+++}$ ,  $\text{Cu}^{++}$ ,  $\text{Cd}^{++}$ ,  $\text{Sn}^{++}$ ,  $\text{Sn}^{++++}$ ,  $\text{As}^{+++}$ ,  $\text{H}_2\text{AsO}_3^-$ ,  $\text{AsO}_4^{--}$ ,  $\text{Sb}^{+++}$ ,  $\text{Fe}^{++}$ ,  $\text{Fe}^{+++}$ ,  $\text{Al}^{+++}$ ,  $\text{Cr}^{+++}$ ,  $\text{Mn}^{++}$ ,  $\text{Zn}^{++}$ ,  $\text{Ni}^{++}$ ,  $\text{Co}^{++}$ ,  $\text{Ca}^{++}$ ,  $\text{Ba}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{NH}_4^+$ .



\* A bracketed formula [cold HCl] means that the substance (HCl in this case) is added as a reagent.

\*\* The notation || means separation by centrifuging and decanting. The double vertical parallel lines at the left refer to the precipitate and the one vertical line at the right refers to the decantate.

#### OUTLINE 1: THE SEPARATION OF CATIONS INTO GROUPS

the colors and other characteristics of the solutions and precipitates that make the identification of the various cations possible, the following program will be followed. Practice solutions ("known" solutions) containing all the cations of each individual group will first be analyzed. The known solution for a given group will then be followed by the unknown solution (or solid) for that group, in which the student goes through the same steps that he has taken with the known. The series of group knowns and unknowns will be followed by an unknown that contains combinations of all four cation groups in the form of an alloy.

Thus, bit by bit, the separation and identification of the metallic ions will be studied. The student will then be ready to extend his efforts to the study of the identification of anions. This he will do by analyzing salts and salt mixtures.

In keeping with this objective of studying the qualitative procedures of the separate groups before undertaking a complete analysis, the following substances will be analyzed and in the following order:

### SCHEDULE OF LABORATORY WORK

1. *One silver group known.* This solution contains all the cations of the silver group. It will not contain cations of other groups. Obtain it and all subsequent knowns from the instructor. Follow the directions given in Procedures 1 to 4, inclusive.

2. *One or two silver group unknowns.* These solutions contain cations of the silver group. They will not contain cations of other groups. Obtain these and all subsequent unknowns from the instructor. Follow the directions given in Procedures 1 to 4, inclusive.

3. *One copper-arsenic group known.* This solution contains all of the cations of the copper-arsenic group. It will not contain cations of other groups. Follow the directions given in Procedures 5 to 14, inclusive.

4. *One or two copper-arsenic group unknowns.* These solutions contain cations of the copper-arsenic group. They will

not contain cations of other groups. Follow the directions given in Procedures 5 to 14, inclusive.

5. *One aluminum-nickel group known.* This solution contains all the cations of the aluminum-nickel group and will not contain cations of other groups. Follow the directions given in Procedures 15 to 21, inclusive.

6. *One or two aluminum-nickel group unknowns.* These solutions contain cations of the aluminum-nickel group. They will not contain cations of other groups. Analyze according to the directions given in Procedures 15 to 21, inclusive.

#### NOTE

In the presence of phosphates or borates, a modified plan of analysis must be used for the aluminum-nickel group. Unknowns ordinarily issued in the course will not contain phosphates or borates that necessitate using the modified procedure.

7. *One barium-magnesium group known.* This solution contains all of the cations of the barium-magnesium group. It will not contain cations of other groups. Follow the directions given in Procedures 22 to 27, inclusive.

8. *One or two barium-magnesium group unknowns.* These solutions contain cations of the barium-magnesium group. They will not contain cations of other groups. Analyze according to the directions given in Procedures 22 to 27, inclusive.

9. *One alloy.* This solid may contain any or all of the 21 metals. Follow the directions given in Procedure 28.

10. *Preliminary tests and specific tests for anions.* Follow the directions given in Experiments 1, 2, 3, and 4, pages 137, 140, 144, and 150.

11. *Complete analysis of solids for both metallic ions and acid radicals.* The remainder of the laboratory work will consist in the complete analysis of solid unknowns for cations and anions. Follow the directions given in Chapter 10.

## RECORD OF LABORATORY WORK AND LABORATORY REPORTS

A record of all laboratory work is to be kept on the blank pages at the end of each chapter in this manual in accordance with the following directions:

1. As each group known or unknown is being analyzed, the outline for that group must be developed in the manual. This outline is similar to those printed in this manual. The object of making such an outline is to enable the student to visualize the steps of the analysis and record his own findings. Each step in the outline must be recorded concurrently with the actual laboratory performance of that step.

2. All confirmatory tests obtained in the analysis of a group known must be approved by the instructor. Confirmatory tests obtained in the analysis of an unknown need not be thus approved.

3. The group known must be finished and the completed outline for this group known must be approved by the instructor before an unknown can be issued. The student must demonstrate to the instructor that he is familiar with the analysis of the group before he is permitted to start the analysis of the unknown.

4. When a group unknown is reported to the instructor, the manual must contain:

- (a) The approved outline of the group known.
- (b) All equations for the group known.
- (c) The outline for the unknown.

5. The alloy will not be issued until the student is able to demonstrate to his instructor a proper understanding of the analysis of the alloy.

6. When the alloy is reported, the manual must contain:

- (a) A composite outline showing how it was analyzed.
- (b) Equations for dissolving the metals proved to be present in the alloy.



7. Salts and salt mixtures will be reported in accordance with the instructions given in Chapter 11.

8. The first salt will not be issued until the student can demonstrate a satisfactory understanding of its plan of analysis. Experiments 1, 2, 3, and 4, pages 137, 140, 144, and 150, must be performed before the first salt or salt mixture is analyzed.

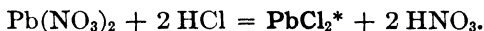
9. Special solids will be reported in the same manner as salts.

## CHAPTER 2

### Solutions and Solubility

FROM WHAT has been stated in Chapter 1, it is evident that the whole plan of separation of ions is based on the solubilities of the various compounds formed by these ions. The identification of cations and anions involves a series of processes of solution and precipitation in which the element or radical in question eventually appears as a precipitate or as a solution of distinctive color. Qualitative analysis is thus largely concerned with solutions, solubility, and the formation of precipitates. It is concerned with the best conditions for the formation of precipitates and the best conditions for the separation of one ion from another.

Suppose, in a solution containing lead nitrate and sodium nitrate, that it is necessary to separate the lead ions from the sodium ions. The method of procedure would be to add some substance which would form a precipitate with the dissolved lead ions but which would not form a precipitate with the sodium ions. For this purpose hydrochloric acid could be used; it reacts with lead nitrate as follows:

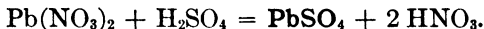


The sodium ions would remain in solution but most of the lead ions would precipitate as insoluble lead chloride. Some of the lead, however, would remain dissolved because  $\text{PbCl}_2$  is somewhat soluble in water, so that the separation of lead and sodium would not be complete.

It would be much more satisfactory to use as a precipitating reagent some substance which would form a more insoluble lead compound. Such a substance is sulfuric acid or any compound that forms the sulfate ion in solution:

---

\* **Boldface** type indicates a solid, usually a precipitate.



In this case almost all the lead would be removed, as shown by the figures for the solubility of  $\text{PbSO}_4$  in water at  $25^\circ$ :

100 cc. of water at  $25^\circ$  dissolves 0.004 g. of  $\text{PbSO}_4$ .

100 cc. of water at  $25^\circ$  dissolves 0.9 g. of  $\text{PbCl}_2$ .

A certain infinitesimal amount of lead would still remain in the solution, but the amount would be so small that it could be disregarded.

If the solution from which the lead was precipitated had been heated to  $100^\circ$ , slightly more  $\text{PbSO}_4$  would have remained in solution because  $\text{PbSO}_4$  is somewhat more soluble in hot than in cold water. If a slight excess of  $\text{H}_2\text{SO}_4$ , that is, more than was necessary to precipitate all the lead, were used in this precipitation, the  $\text{PbSO}_4$  would be still more insoluble. To get the best separation, we should:

- (a) Precipitate the lead as  $\text{PbSO}_4$ .
- (b) Precipitate the lead from a cold solution.
- (c) Use an excess of the precipitating reagent ( $\text{H}_2\text{SO}_4$ ).

In the separation of substances, then, the attempt is made to carry out the precipitation under conditions which make the precipitate as insoluble as possible. For intelligent analytical work it is necessary that the student should understand what these conditions are. This understanding necessitates a knowledge of some of the properties of solutions.

### SATURATED SOLUTIONS\*

When a solid is immersed in a liquid in which it is soluble, molecules of the solute begin to escape into the solvent. The amount dissolved will depend on:

- (a) The attraction between the solvent and the solute.
- (b) The temperature at which the dissolving takes place.

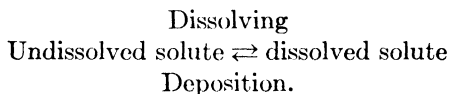
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\* To understand the following discussion, the student should review the fundamental theories of elementary chemistry, especially the material dealing with equilibrium reactions, ionization, and colloids.

The rate at which solution takes place depends on the fineness of division and the bringing of fresh portions of the solvent in contact with the solute. Lump sugar dissolves in water at a certain rate. If powdered, it dissolves faster, and still faster if the solution is stirred.

If a compound such as alum is added to a given volume of water at a given temperature, the water will dissolve the alum until a certain concentration is reached, after which no more alum will dissolve. The solution is said to be *saturated* at that particular temperature. As long as the solvent at a given temperature will dissolve more solute, the solution is said to be *unsaturated*.

A saturated solution is defined as *a solution in which the solution and the solute are in equilibrium at a given temperature*. To get a picture of this condition, suppose we visualize a lump of sugar dissolving in water at a certain temperature. The molecules of sugar are attracted by the solvent and keep leaving the solid. But there is also an attraction between the crystal and the solute. The crystal attracts molecules of solute to its surface so that just as soon as the substance begins to dissolve, molecules of solute begin to deposit on the solid. The relation may be represented thus:



The process of dissolving is represented by the upper arrow; the process of deposition is indicated by the lower arrow. At the outset dissolving is faster than deposition, but as more substance is dissolved the rate of solution is slower and the rate of deposition faster. Eventually the two processes become equal in speed, equilibrium is reached, and the solution is in equilibrium with the solute and is said to be saturated. It is possible to disturb this equilibrium by:

- (a) Adding more of the solvent.
- (b) Increasing or decreasing the temperature.
- (c) Adding a third substance.

The last case is of especial importance in chemical analysis and will be discussed under the Common Ion Effect, page 25.

When a substance is precipitated from solution, the remaining solution contains a small amount of the substance that was precipitated, this amount varying with the particular substance. The solution is saturated with the precipitate and is therefore in equilibrium with it. The figures given for the solubility of  $\text{PbCl}_2$  and  $\text{PbSO}_4$  represent saturated solutions in which the two solutions at the particular temperature are in equilibrium with solid  $\text{PbCl}_2$  and  $\text{PbSO}_4$ , respectively.

### SUPERSATURATED SOLUTIONS

In the case of saturated solutions of substances whose solubilities increase with rise in temperature, a lowering of the temperature of the solution is usually attended with a separation of solute, thus forming a saturated solution at the new lower temperature. Under certain conditions, however, it is possible to lower the temperature of such a saturated solution without the separation of crystals of the solute. In order to bring this condition about, the solid phase (crystals of the solute) must not be present. The resulting solution is said to be *supersaturated*.

To illustrate, if a saturated solution of borax, alum, or sodium sulfate is prepared and any remaining crystals of these compounds are removed by decantation or filtration, this solution can usually be cooled several degrees without separation of the solid phase. It is supersaturated and in a state of pseudo equilibrium in which a kind of passive resistance to the formation of crystals seems to exist. The formation of crystals may often be brought about by shaking, vigorous stirring, or rubbing the inside of the beaker with the end of a glass rod. The addition of some of the solid phase always brings the solution to equilibrium. An example of this kind which is of interest in qualitative analysis will be encountered in the test for magnesium (Procedure 25), in which the solution often becomes supersaturated with  $\text{MgNH}_4\text{PO}_4$ .

## PERCENTAGE, MOLAR AND NORMAL SOLUTIONS

A knowledge of the amount of solute present in a given solution is of great importance in almost all fields of chemistry. In order that such information may be available, solutions are prepared which have a definite concentration. "Concentration" in this case has a quantitative significance; it refers to the ratio of the amount of dissolved substance either to the volume or weight of the solution or to the volume or weight of the solvent.

The amount of dissolved substance in a given quantity of solution is expressed in a variety of units. Some of those in common use are grams, percentages, moles, formula weights, and equivalent weights.

**Percentage strength.** In notations of this kind the ratio of the weight of the solute to that of the solution is expressed in parts per 100.

A 5 per cent solution of common salt is one in which 100 g. of the solution contains 5 g. of NaCl; that is, there will be 95 g. of water (approximately 95 cc.) and 5 g. of sodium chloride. To prepare such a solution, three methods are used:

(a) Dissolve 5 g. of NaCl in enough water to make a total volume of 100 cc.

(b) Dissolve 5 g. of NaCl in 95 cc. of water.

(c) Add 95 g. of water to 5 g. of NaCl.

In Methods (b) and (c) the total volume of the solution will not be exactly 100 cc.

Method (c) is the only one that gives a strictly 5 per cent solution. But if we had such a solution and wished to obtain 1 g. of NaCl it would be necessary to weigh out accurately 20 g. of the solution, which would be a nuisance.

Method (a) is frequently used and has the advantage that a desired amount of salt can be obtained by accurately measuring a given volume of the solution. If we wish 0.5 g. of salt, it is simply necessary to take 10 cc. of the solution by means of a pipette or a burette.

**Molar solutions.** Because the properties of so many solutions depend on the number of molecules in a given volume of the solvent, it is often convenient to express the concentration in terms of the number of gram molecular weights (moles) in 1000 cc. of the solution. A molar solution contains one mole (one gram molecular weight) of solute in one liter of solution. The molecular weight of sulfuric acid is 98. A molar solution contains 98 g. in 1 liter of the solution (not 98 g. in 1000 cc. of the solvent, which is quite different). Similarly, a molar solution of HCl contains 36.46 g. per liter, and a molar solution of cane sugar ( $C_{12}H_{22}O_{11}$ ) contains 342 g. in a liter.

This system obviously permits a solution of any concentration to be expressed in terms of molarity. Thus a solution of 80 g. of NaOH per liter is 2 molar and one containing 0.8 g. per liter is .02 molar.

*Problem:* 0.5 g. of  $K_2SO_4$  is present in 200 cc. of a solution. What is the molarity of the solution?

When the concentrations of very dilute solutions are expressed in terms of molarity, the resulting values are sometimes very small. At  $20^\circ$ , one liter of water dissolves 0.00233 g. of  $BaSO_4$ . The molecular weight of  $BaSO_4$  is 233; consequently,  $0.00233/233 = .00001$  mole of  $BaSO_4$  per liter. The solution is therefore 0.00001 molar. Sometimes this notation is shortened by writing it  $0.0_41$ . More frequently, however, such solubilities are expressed by the use of negative exponents:

$$0.00001 \text{ molar is } \frac{1}{100,000} \text{ or } 1 \times 10^{-5} \text{ molar.}$$

*Example.* At  $25^\circ$  a saturated solution of AgCl contains 2 mgm. per liter. Calculate the molarity of the solution. (The molecular weight of AgCl is 142.5.)

$$\frac{0.002}{142.5} = 0.000014 \text{ molar, or } 1.4 \times 10^{-5} \text{ molar.}$$

It is often desirable to describe a solution in terms of its ionic concentrations. For this purpose the term *gram ion* may be used. Suppose 1 mole of  $\text{CuSO}_4$  (159.6 g.) has been dissolved in water and made up to 1 liter. If we assume 100 per cent dissociation, the solution contains 1 gram ion (63.6 g.) of copper ions and 1 gram ion (96 g.) of sulfate ions.

### Problems

1. How many grams of each of the following substances must be taken to make 0.5 liter of a molar solution?  $\text{Cl}_2$ ;  $\text{FeCl}_3$ ;  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ;  $\text{Cu}(\text{NH}_3)_4\text{SO}_4$ ?
2. Calculate the molar concentration of a nitric acid solution which contains 378 g. of solute per liter of solution.
3. One liter of a saturated  $\text{AgNO}_3$  solution at  $20^\circ$  contains 2091 g. of the solute. Calculate its molarity.
4. If the molar solubility of  $\text{KClO}_3$  at a certain temperature is 0.52, how many grams of the salt are present in 250 cc. of the solution?
5. From the following solubilities (grams in 100 cc. of solution), calculate the molarity of the solutions, using negative exponents in each case. Calculate also the number of milligrams of solute in 1000 cc. of the saturated solution of each.

$\text{BaSO}_4$ . . . . .	$2 \times 10^{-2}$
$\text{CaCO}_3$ . . . . .	$1.3 \times 10^{-3}$
$\text{Mg}(\text{OH})_2$ . . . . .	$9 \times 10^{-4}$
$\text{MnS}$ . . . . .	$3.3 \times 10^{-5}$
$\text{AgI}$ . . . . .	$3.5 \times 10^{-7}$

**Normal solutions.** With acids, bases, and salts, the concentrations of the solutions are commonly expressed in terms of normality.

**Acids:** A normal solution of an acid contains 1 gram atom (1 g.)\* of hydrogen in a liter of solution. For  $\text{HCl}$  such a solution would require 36.46 g. of the acid, whereas for sulfuric acid,  $\text{H}_2\text{SO}_4$  (mol. wt. 98), 49 g. of acid would be required to furnish 1 g. of hydrogen. Similarly with orthophosphoric acid,  $\text{H}_3\text{PO}_4$  (mol. wt. 98),  $\frac{98}{3}$  g. of acid would be necessary, whereas with pyrophosphoric acid,  $\text{H}_4\text{P}_2\text{O}_7$ , one-fourth the molecular

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\* Strictly speaking, this value is 1.008.



weight of the acid dissolved in one liter of solution would furnish a normal solution of this acid.

*Bases:* The active part of the base is the OH group. A normal solution of a base contains 17 g. of hydroxyl (OH) per liter of solution. In the case of NaOH, 40 g. per liter would provide a normal solution; with  $\text{Ba}(\text{OH})_2$ , one-half the molecular weight would be needed.

*Salts:* The weight of solute in a liter of normal solution of a salt is determined by dividing the molecular weight of the salt by the total valence of the negative radical. A normal solution of NaCl contains 58.46 g. of the salt per liter, and a normal solution of  $\text{CaCl}_2$  contains 55.46 g. per liter.

### NOTE

This method of calculating the amount of solute necessary for a normal solution does not hold when the solute is used as an oxidizing or reducing agent. For the preparation of solutions of that type, consult a text on quantitative analysis.

### MOLAR AND NORMAL SOLUTIONS

(Grams of solute per liter)

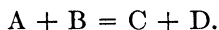
<i>Name of Substance</i>	<i>Formula</i>	<i>Molar</i>	<i>Normal</i>
Hydrogen chloride . . . . .	HCl	36.46	36.46
Sulfuric acid . . . . .	$\text{H}_2\text{SO}_4$	98.0	49.0
Acetic acid. . . . .	$\text{H}(\text{C}_2\text{H}_3\text{O}_2)$	60.0	60.0
Sodium hydroxide . . . . .	NaOH	40.0	40.0
Potassium hydroxide . . . . .	KOH	56.0	56.0
Sodium chloride . . . . .	NaCl	58.46	58.46
Sodium carbonate . . . . .	$\text{Na}_2\text{CO}_3$	106.0	53.0
Sodium bicarbonate . . . . .	$\text{NaHCO}_3$	84.0	84.0
Aluminum nitrate . . . . .	$\text{Al}(\text{NO}_3)_3$	213.0	71.0
Copper sulfate . . . . .	$\text{CuSO}_4$	159.6	79.8

### THE LAW OF MASS ACTION

When two substances which can react with each other are brought together in solution, a definite time interval is necessary for the reaction to take place. This time interval may be as small as 1/100,000 of a second, so that it is impossible to measure it. In other cases, days or even years may be required

for the reaction to become completed. The reaction rate is influenced by certain factors, some of the more important of which are temperature, catalysts, and concentration of reactants.

The influence of concentration of reactants has been extensively studied and can be expressed in mathematical form. Consider the case in which two substances A and B react to form two products C and D. Then



The reaction cannot take place unless the reacting molecules come in contact. The rate at which the reaction takes place will then depend upon the number of impacts of molecules of A and molecules of B per second. If  $x$  molecules of A and  $x$  molecules of B are dissolved in 1000 cc. of water, the reaction will be much slower than when  $x$  molecules of each are dissolved in 100 cc. because in the latter case the molecules will not have to travel so far to come together and react.

Suppose that in 100 cc. we double the number of molecules of A so that we have  $2x$  molecules of A and  $x$  molecules of B. It is evident that the products C and D will be formed faster because the solution now contains twice as many molecules of A, and the probability that a molecule of A will encounter a molecule of B is greater than when the two were present in equal numbers. A mason will build a wall much faster if more than enough bricks are at hand and he does not have to move around to get them.

This effect of the excess of A is *mass action*. We may consider this phase of mass action as the effect produced upon the speed of a reaction by the presence of an available excess of one of the substances taking part in the reaction.

In 1867 Guldberg and Waage expressed the law of mass action as follows: *The speed of a chemical reaction is proportional to the molecular concentrations of the reacting molecules.* As units for expressing concentration it is necessary to use,

for each reacting substance, the number of gram molecular weights (moles) per liter.

In the reaction  $\text{H}_2 + \text{Cl}_2 = 2 \text{HCl}$ , the speed of the reaction is proportional to the molecular concentration of  $\text{H}_2$  and  $\text{Cl}_2$  expressed as follows:

$$\text{Speed} \propto [\text{H}_2] \times [\text{Cl}_2] \quad (\propto \text{ means proportional}).^*$$

This does not mean that the speed is *equal* to  $[\text{H}_2] \times [\text{Cl}_2]$ .

The above relationship may, however, be expressed in the form of an equation as follows:

$$\text{Speed} = k \times [\text{H}_2] \times [\text{Cl}_2],$$

in which  $k$  is a constant, called the *velocity constant*. If the concentrations of  $\text{H}_2$  and  $\text{Cl}_2$  are 1 mole per liter, then

$$\text{Speed} = k \times 1 \times 1 = k.$$

If the concentration of  $\text{H}_2$  is 2 and  $\text{Cl}_2$  is 3 moles per liter, then

$$\text{Speed} = k \times 2 \times 3 = 6k,$$

or six times the speed in the first case.

In the reaction  $\text{H}_2 + \text{H}_2 + \text{H}_2 + \text{N}_2 = 2 \text{NH}_3$ ,

the speed is not proportional to the concentration of hydrogen molecules but to  $[\text{H}_2] \times [\text{H}_2] \times [\text{H}_2] \times [\text{N}_2]$ , so that we have the equation

$$\text{Speed} = k \times [\text{H}_2]^3 \times [\text{N}_2].$$

In the reaction  $2\text{H}_2\text{S} + 3\text{O}_2 = 2\text{H}_2\text{O} + 2\text{SO}_2$ ,

$$\text{Speed} = k \times [\text{H}_2\text{S}]^2 \times [\text{O}_2]^3.$$

The velocity constant  $k$  has different values for the three reactions illustrated because we are using different substances in each case.

The following analogy may help to illustrate the meaning of  $k$ . The speed with which a man walks depends on (a) the

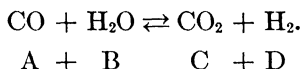
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\* The notation [ ] always refers to concentration expressed in either moles per liter or, in the case of ionic equilibria, gram ions per liter. In this particular case  $[\text{H}_2]$  and  $[\text{Cl}_2]$  refer to moles of  $\text{H}_2$  and moles of  $\text{Cl}_2$ , respectively, per liter.

length of his steps and (b) their rapidity. It is therefore proportional to the product of the two. But his speed is not equal to the product until we agree on the length of his steps and the rapidity (the number of steps in a given time interval). This can be expressed as follows:

Speed = (length of step)  $\times$  (rapidity)  $\times k$ , in which  $k$  is a constant made up of feet and minutes.

**Equilibrium in balanced reactions.** Using A and B to indicate reacting molecules, let us consider a reaction in which the products are capable of reacting with each other and begin to do so as soon as they are formed. A familiar example is the gas phase reaction between carbon monoxide and steam where the products,  $\text{CO}_2$  and  $\text{H}_2$  react with each other as indicated by the lower arrow:



This type of reaction is sometimes called a *balanced* or an *equilibrium reaction*.

The speed ( $S_1$ ) of the reaction to the right  $\rightarrow$  is represented thus:

$$S_1 = [\text{A}] \times [\text{B}] \times k_1.$$

The speed ( $S_2$ ) of the reverse reaction (to the left  $\leftarrow$ ) is

$$S_2 = [\text{C}] \times [\text{D}] \times k_2.$$

$k_1$  and  $k_2$  are velocity constants for the two reactions.

At the start of the reaction A and B are present in high concentrations, but they are gradually used up as the reaction progresses so that the speed to the right gradually decreases.

At the beginning of the reaction, C and D are present in small amounts, but they increase in concentration as the reaction progresses so that the speed to the left gradually increases. At equilibrium the two speeds are equal; that is,

$$S_1 = S_2.$$

Consequently,  $[\text{A}] \times [\text{B}] \times k_1 = [\text{C}] \times [\text{D}] \times k_2$ .

Dividing each side of the equation by  $[A] \times [B] \times k_2$  gives

$$\frac{k_1}{k_2} = \frac{[C] \times [D]}{[A] \times [B]}.$$

Since  $k_1$  and  $k_2$  are both constants, it is possible to represent them by  $K$ , a new constant, so that we have

$$K = \frac{[C] \times [D]}{[A] \times [B]}.$$

$K$  is called the *equilibrium constant*.

The equilibrium constant is a numerical value of great importance in chemistry. It can be determined experimentally in the laboratory by making an analysis to find the concentrations of the substances in the solution at equilibrium.

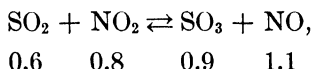
To illustrate the application of the above formula to a specific case, suppose that we have 3 moles of CO and 2 moles of H<sub>2</sub>O in a liter at the beginning of the reaction. After equilibrium is reached it is found by experiment that the concentration of the H<sub>2</sub> in the system is 1 mole per liter. Then at equilibrium the concentrations of the four substances, expressed in moles per liter, are

$$\text{H}_2 = 1, \quad \text{CO} = 2, \quad \text{H}_2\text{O} = 1, \quad \text{CO}_2 = 1.$$

The equilibrium constant is

$$K = \frac{1 \times 1}{2 \times 1} = \frac{1}{2} = 0.5.$$

As another illustration consider the reaction



with concentrations of the reactants and the products at equilibrium expressed in moles per liter. Here

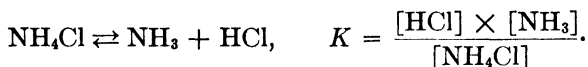
$$K = \frac{0.9 \times 1.1}{0.6 \times 0.8} = 2.06.$$

If we set up a system in which the  $\text{SO}_2$ ,  $\text{NO}_2$ ,  $\text{SO}_3$ , and  $\text{NO}$  are introduced in proportions other than those given above, the reaction will proceed until the four substances attain concentration values that once more give  $K = 2.06$ .

Suppose we increase the concentration of  $\text{NO}_2$ . Then the concentrations of the other substances must change. At equilibrium the concentration of  $\text{SO}_2$  will necessarily become smaller if the value 2.06 is constant, and the concentrations of  $\text{NO}$  and  $\text{SO}_3$  will be increased.

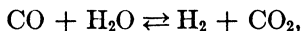
In many chemical operations we often add a large excess of one reagent to push the reaction as near to completion as possible.

Other equilibrium equations may be illustrated as follows:



The student should appreciate the fact that the equilibrium constant has a definite numerical value. It is a constant of nature which possesses certain fundamental characteristics, some of which are as follows:

1. At constant temperature the numerical value is independent of the original concentrations of the reactants, which means that in a reaction of the type



the equilibrium constant in the systems containing, originally,

0.3 mole of  $\text{H}_2\text{O}$  and 0.3 mole of  $\text{CO}$

0.6 mole of  $\text{H}_2\text{O}$  and 0.3 mole of  $\text{CO}$

0.3 mole of  $\text{H}_2\text{O}$  and 0.6 mole of  $\text{CO}$

0.6 mole of  $\text{H}_2\text{O}$  and 0.1 mole of  $\text{CO}$

will be the same. The difference in the four systems will consist of different concentrations of the four substances at equilibrium. They will necessarily be different in the four cases if the value

$$\frac{[\text{H}_2] \times [\text{CO}_2]}{[\text{CO}] \times [\text{H}_2\text{O}]} = \text{constant.}$$

2. The equilibrium constant is different for different reactions.

3. The larger the equilibrium constant, the more complete the reaction.

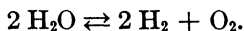
4. The equilibrium constant for a given reaction is different for different temperatures.

5. The equilibrium constant is not changed by the presence of a catalyst.

6. The same state of equilibrium is reached whether the reaction is approached from the right or from the left. Thus if 1 mole of CO and 1 mole of H<sub>2</sub>O are brought together in a given volume and at a given temperature, at equilibrium definite concentrations of the four substances will result. If the system is prepared by using 1 mole of H<sub>2</sub> and 1 mole of CO<sub>2</sub> in the same volume and at the same temperature the same state of equilibrium will be reached.

## IONIZATION EQUILIBRIUM

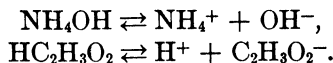
**Ionic equilibria.** In the discussion of balanced reactions an equation for the equilibrium constant was developed, based upon the law of mass action. The dissociation of water by heat, often spoken of as the *thermal dissociation* of water, is expressed by the equation



The equation for the equilibrium constant is

$$K = \frac{[\text{H}_2]^2 \times [\text{O}_2]}{[\text{H}_2\text{O}]^2}.$$

In the study of the theory of ionization, it was shown that substances which undergo partial ionization in solution exist in a state of equilibrium between ions and non-ionized molecules. They are expressed by balanced reactions:



Just as in the thermal dissociation of water, the law of mass action can be used to calculate equilibrium constants for electrolytic dissociation. For the above cases the equilibrium constants would be

$$K = \frac{[\text{NH}_4^+] \times [\text{OH}^-]}{[\text{NH}_4\text{OH}]}$$

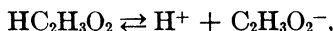
and

$$K = \frac{[\text{H}^+] \times [\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}.$$

In reactions of this kind,  $K$  is called the *ionization* or *dissociation constant*.

As in the case of the equilibrium constants already discussed the ionization constant can be calculated if the concentrations of ions in the solution are known. For example:

In a 0.1 molar solution of acetic acid, which dissociates according to the equation



the acid is ionized to the extent of only 1.34 per cent. The reaction is therefore only 1.34 per cent complete. The concentration of ions and molecules in the solution is

$\text{HC}_2\text{H}_3\text{O}_2$ (molecules)	$0.1 \times 98.66\% = 0.09866$ mole per liter.
Hydrogen ion ( $\text{H}^+$ )	$0.1 \times 1.34\% = 0.00134$ gram ion per liter.
Acetate ion ( $\text{C}_2\text{H}_3\text{O}_2^-$ )	$0.1 \times 1.34\% = 0.00134$ gram ion per liter.

The equilibrium constant is

$$K = \frac{0.00134 \times 0.00134}{0.09866} = 0.0000182 = 1.82 \times 10^{-5}.$$

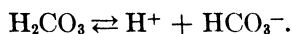
This value of  $K$  (ionization constant) is a measure of the tendency of acetic acid to ionize. In the case of acids the ionization constant is a measure of the strength of the acid. The larger the constant, the greater the hydrogen ion concentration, and consequently the stronger the acid. This relationship



is shown in the following table, which gives values of the ionization constants of several acids at 25°.

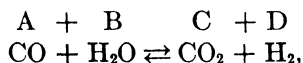
<i>Acid</i>	<i>Ionization Constant</i>
Iodic.....	$2 \times 10^{-1}$
Formic.....	$2.1 \times 10^{-4}$
Acetic.....	$1.8 \times 10^{-5}$
Carbonic ( $k_1$ ).....	$3 \times 10^{-7}$
Carbonic ( $k_2$ ).....	$6 \times 10^{-11}$

In carbonic acid,  $k_1$  represents the ionization constant of the hydrogen ion formed according to the equation



The ionization constant of the second hydrogen atom, obtained for example by the hydrogen ion concentration in  $\text{NaHCO}_3$ , is represented by  $k_2$ .

**The common ion effect.** If the concentration of any ion in a given solution is changed, the equilibrium will be upset, just as it is in the case of the molecular equation



where it was shown that if the number of molecules of  $\text{H}_2\text{O}$  (B) are doubled, the value of  $K$  does not change, but the amounts of A, C, and D change. This principle finds application in reducing the acidity of solutions of weak acids and the alkalinity of weak bases.

*Weak acids.* If sodium acetate crystals are added to an acetic acid solution, the concentration of acetate ions in the solution will be increased because the sodium acetate is completely ionized:



and furnishes acetate ions. To keep  $K$  constant, the other factor,  $[\text{H}^+]$ , in the numerator of the formula

$$\frac{[\text{H}^+] \times [\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = K$$

must become smaller or the denominator larger. Both effects occur. In other words, the addition of the sodium acetate has the following effects:

- (a) Increases the acetate ion concentration.
- (b) Decreases the  $H^+$  concentration.
- (c) Increases the concentration of undissociated molecules.

The effect of increasing the acetate ion concentration in a solution of acetic acid is shown by the following data:

A 0.1 molar solution of acetic acid is 1.34 per cent ionized.

A 0.1 molar solution of sodium acetate is 100 per cent ionized.

Dissolving 8.2 g. of sodium acetate (enough to make 1 liter of solution 0.1 molar) in 1 liter of 0.1 molar acetic acid solution will decrease the degree of ionization from 1.34 to 0.02 per cent. This change in ionization caused by the addition of acetate ions is an example of the *common ion effect*.

The calculation is carried out as follows: The acetic acid is 1.34 per cent ionized so the concentration of each ion is 0.00134 gram ion per liter.

$$K = \frac{0.00134 \times 0.00134}{0.0987} = 0.0000182.$$

Since the  $NaC_2H_3O_2$  is completely ionized we will have added 0.1 gram ion of acetate, and the total acetate ion concentration is  $0.00134 + 0.1 = 0.10134$ . In reestablishing equilibrium, a certain number of hydrogen ions and an equal number of acetate ions will combine to form acetic acid molecules. Call this number  $x$ . Then the new equilibrium is expressed as follows:

$$\frac{(0.00134 - x)(0.10134 - x)}{(0.0987 + x)} = 0.0000182.$$

Solving the equation for  $x$  gives  $x = 0.00132$ . The hydrogen ion concentration is now  $0.00134 - 0.00132 = 0.00002$  gram ion per liter. The acidity (hydrogen ion concentration) of any weak acid is always decreased by the presence of a soluble salt of the acid.

**Weak bases.** It is possible to reduce the alkalinity of a solution of a weak base, such as  $NH_4OH$ , by the addition of a common ion.  $NH_4OH$  is ionized as follows:



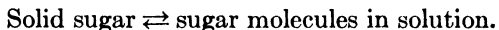
The addition of an ammonium salt, such as  $\text{NH}_4\text{Cl}$ , to a solution of  $\text{NH}_4\text{OH}$  reduces the concentration of the  $\text{OH}^-$  ions because this salt is completely ionized,



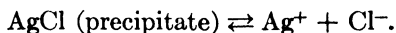
and consequently furnishes a high concentration of  $\text{NH}_4^+$  ions. This condition reduces the alkalinity of the  $\text{NH}_4\text{OH}$  solution just as the addition of acetate ions reduces the acidity of a solution of acetic acid.

### THE SOLUBILITY PRODUCT

When a saturated solution of the nonelectrolyte sugar is prepared by shaking an excess of sugar with water, the following equilibrium exists:



When a saturated solution of a very slightly soluble salt, such as  $\text{AgCl}$ , is prepared by shaking excess  $\text{AgCl}$  with water, a somewhat different situation exists.  $\text{AgCl}$  is a salt; hence it is 100 per cent ionized. Therefore, the saturated solution in equilibrium with solid  $\text{AgCl}$  contains silver ions and chloride ions but no undissociated  $\text{AgCl}$  molecules. In other words, the  $\text{Ag}^+$  ions and  $\text{Cl}^-$  ions are in equilibrium with a precipitate of  $\text{AgCl}$ . We may, therefore, represent the equilibrium conditions in such a saturated solution of  $\text{AgCl}$  as follows:



Since this is a true equilibrium, an equilibrium constant  $K$  may be expressed as follows:

$$K = \frac{[\text{Ag}^+] \times [\text{Cl}^-]}{\text{AgCl (precipitate)}}.$$

But we know from the behavior of solutions that the amount of excess solute in equilibrium with a saturated solution at a given temperature has no effect on the concentration of the

solution; the amount of solute in solution will be the same whether we have a mere speck of excess solute or a very large amount of excess solute. In other words, the concentration of  $\text{Ag}^+$  and  $\text{Cl}^-$  in the above system is independent of the amount of  $\text{AgCl}$  precipitate. Obviously, then, we should leave the " $\text{AgCl}$  (precipitate)" out of the equation entirely. The equation then becomes

$$K = [\text{Ag}^+] \times [\text{Cl}^-].$$

This equation tells us, simply, that the product of the concentration (in gram ions per liter) of the solute ions in a saturated solution of a very slightly soluble electrolyte is constant at any given temperature. This constant,  $K$ , is called the *solubility product constant* or simply the *solubility product*, and is usually designated by the term  $K_{s.p.}$  or, very commonly, S.P.

The solubility product is the product of the concentrations of the solute ions present in a saturated solution. In other words, in a saturated solution the product of the concentration of the ions is just equal to  $K_{s.p.}$ , and the solubility product,  $K_{s.p.}$ , is just satisfied. If the product of the concentration of the ions is greater than  $K_{s.p.}$  the solution is supersaturated; if less than  $K_{s.p.}$ , the solution is unsaturated.

To state the principle more specifically: If the concentration of silver ions and the concentration of chloride ions (expressed in gram ions per liter) in a liter of solution is such that their product is less than  $K_{s.p.}$  for  $\text{AgCl}$  or is just barely equal to  $K_{s.p.}$ , no precipitate of  $\text{AgCl}$  will form. If the product of the concentration of the silver ions and the chloride ions is greater than  $K_{s.p.}$  a precipitate of  $\text{AgCl}$  will form; furthermore,  $\text{AgCl}$  will keep precipitating until enough  $\text{Ag}^+$  ions and  $\text{Cl}^-$  ions have been removed to reduce the concentration of the  $\text{Ag}^+$  ions and  $\text{Cl}^-$  ions remaining in solution to such values that their product will just equal  $K_{s.p.}$ .

**The calculation of solubility products.** The solubility product of a typical "insoluble" salt such as  $\text{BaSO}_4$  is calculated as follows: A saturated solution of  $\text{BaSO}_4$  was found to con-

tain  $1 \times 10^{-5}$  moles of  $\text{BaSO}_4$  per liter. Since the  $\text{BaSO}_4$  is 100 per cent ionized, the saturated solution will contain  $1 \times 10^{-5}$  gram ions of  $\text{Ba}^{++}$  and  $1 \times 10^{-5}$  gram ions of  $\text{SO}_4^{--}$  per liter:

$$K_{s.p.} = [\text{Ba}^{++}] \times [\text{SO}_4^{--}] = [1 \times 10^{-5}] \times [1 \times 10^{-5}] = 1 \times 10^{-10}.$$

The solubility product in the above case is calculated for the simplest type of salt, namely, one which yields only two ions from each molecule that dissociates. In its more general form the solubility product formula requires that each ion concentration be raised to a power equal to the number of ions derived from one molecule of the compound. Example:



The solubility of  $\text{Mg}(\text{OH})_2$  is 0.00015 mole per liter. Assuming that the dissolved  $\text{Mg}(\text{OH})_2$  is completely ionized, the  $\text{Mg}^{++}$  ion concentration will be 0.00015 gram ion per liter. The  $\text{OH}^-$  ion concentration will be twice this amount, since each molecule produces two hydroxyl ions:



The solubility product is therefore

$$\begin{aligned} [\text{Mg}^{++}] \times [\text{OH}^-]^2 &= K_{s.p.}, \\ 0.00015 \times (0.0003)^2 &= 1.35 \times 10^{-11}. \end{aligned}$$

In  $\text{AgCl}$  and  $\text{PbCl}_2$  the solubility products are

$$\begin{aligned} [\text{Ag}^+] \times [\text{Cl}^-] &= K_{s.p.} = 1.1 \times 10^{-10}, \\ [\text{Pb}^{++}] \times [\text{Cl}^-]^2 &= K_{s.p.} = 2.4 \times 10^{-4}. \end{aligned}$$

The solubility product is a measure of the relative solubility of the substance, and its numerical value is characteristic of the substance. If the solubility product is a large number, it shows that relatively large concentrations of the ions can exist together in solution; if small, only small concentrations. From the above it is obvious that  $\text{PbCl}_2$  is much more soluble than  $\text{AgCl}$ .

## NOTE

The solubility product formula holds only for slightly soluble ("insoluble") compounds. It does not hold for such moderately soluble salts as NaCl or  $\text{KClO}_3$ , nor does it apply to slightly soluble salts in the presence of high concentrations of foreign salts. In the presence of high concentrations of  $\text{KNO}_3$ , the solubility product constant for  $\text{CaSO}_4$  is found to increase.

## SOLUBILITY PRODUCTS

Silver bromide.....	$[\text{Ag}^+] \times [\text{Br}^-]$	$4 \times 10^{-13}$
Silver chloride.....	$[\text{Ag}^+] \times [\text{Cl}^-]$	$1 \times 10^{-10}$
Silver iodide.....	$[\text{Ag}^+] \times [\text{I}^-]$	$1 \times 10^{-16}$
Barium carbonate.....	$[\text{Ba}^{++}] \times [\text{CO}_3^{--}]$	$7 \times 10^{-9}$
Barium chromate.....	$[\text{Ba}^{++}] \times [\text{CrO}_4^{--}]$	$2 \times 10^{-10}$
Barium sulfate.....	$[\text{Ba}^{++}] \times [\text{SO}_4^{--}]$	$1 \times 10^{-10}$
Calcium carbonate.....	$[\text{Ca}^{++}] \times [\text{CO}_3^{--}]$	$1.2 \times 10^{-8}$
Calcium oxalate.....	$[\text{Ca}^{++}] \times [\text{C}_2\text{O}_4^{--}]$	$2 \times 10^{-9}$
Cadmium sulfide.....	$[\text{Cd}^{++}] \times [\text{S}^{--}]$	$3.6 \times 10^{-29}$
Cobalt sulfide.....	$[\text{Co}^{++}] \times [\text{S}^{--}]$	$3 \times 10^{-26}$
Cupric sulfide.....	$[\text{Cu}^{++}] \times [\text{S}^{--}]$	$8 \times 10^{-45}$
Ferric hydroxide.....	$[\text{Fe}^{+++}] \times [\text{OH}^-]^3$	$1.1 \times 10^{-36}$
Mercuric sulfide.....	$[\text{Hg}^{++}] \times [\text{S}^{--}]$	$4 \times 10^{-53}$
Magnesium hydroxide.....	$[\text{Mg}^{++}] \times [\text{OH}^-]^2$	$1.2 \times 10^{-11}$
Magnesium ammonium phosphate	$[\text{Mg}^{++}] \times [\text{NH}_4^+] \times [\text{PO}_4^{--}]$	$2.5 \times 10^{-13}$
Manganous sulfide.....	$[\text{Mn}^{++}] \times [\text{S}^{--}]$	$1.4 \times 10^{-15}$
Nickel sulfide.....	$[\text{Ni}^{++}] \times [\text{S}^{--}]$	$1.4 \times 10^{-24}$
Lead chloride.....	$[\text{Pb}^{++}] \times [\text{Cl}^-]^2$	$2.4 \times 10^{-4}$
Lead sulfate.....	$[\text{Pb}^{++}] \times [\text{SO}_4^{--}]$	$1 \times 10^{-8}$
Lead chromate.....	$[\text{Pb}^{++}] \times [\text{CrO}_4^{--}]$	$2 \times 10^{-14}$
Lead sulfide.....	$[\text{Pb}^{++}] \times [\text{S}^{--}]$	$4.2 \times 10^{-28}$
Zinc hydroxide.....	$[\text{Zn}^{++}] \times [\text{OH}^-]^2$	$3 \times 10^{-17}$
Zinc sulfide.....	$[\text{Zn}^{++}] \times [\text{S}^{--}]$	$1.2 \times 10^{-22}$

**The formation of precipitates.** When substances are brought together in solution and the product of the concentration of the ions is greater than the solubility product, precipitation occurs.

Suppose that 1 gram ion of silver ions and 1 gram ion of chloride ions are brought together in 1 liter of solution. Since  $K_{s.p.}$  for  $\text{AgCl}$  is  $1 \times 10^{-10}$ , it is evident that the solubility product is greatly exceeded. All but 0.00001 gram ion of silver and all but 0.00001 gram ion of chloride ion will precipitate, or 0.99999 mole of  $\text{AgCl}$  will precipitate.

If the solubility product is not reached, no precipitate will be formed.

One-tenth of a gram ion of silver added to a liter of solution containing  $1 \times 10^{-11}$  gram ion of chlorine will form no precipitate because

$$0.1 \times 1 \times 10^{-11} = 1 \times 10^{-12},$$

and this is less than  $1 \times 10^{-10}$ . Such a solution is unsaturated and can dissolve solid AgCl until the solubility product is reached.

#### NOTE

Under certain conditions the solubility product may be exceeded without a precipitate being formed. An example of this is found in the precipitation of magnesium as magnesium ammonium phosphate ( $K_{s.p.} = 2.5 \times 10^{-13}$ ):



The solubility product is very low, but the rate at which the magnesium ammonium phosphate crystals form is very slow and the solution may not show a precipitate after standing 10 to 12 hours. In this case the solution is supersaturated.

#### Effect of a common ion upon the solubility of a precipitate.

In the precipitation of  $\text{Pb}^{++}$  as  $\text{PbSO}_4$ , the amount of  $\text{PbSO}_4$  left in 1 liter of the solution is 0.0302 g. If an excess of sulfate ions is present, even less  $\text{PbSO}_4$  remains in the solution. This result has been shown experimentally by adding an excess of 0.49 g.  $\text{H}_2\text{SO}_4$  per liter in the precipitation of  $\text{PbSO}_4$ . The solubility of the  $\text{PbSO}_4$  was reduced to 0.0052 g. per liter. Such a result is entirely in accordance with the solubility product principle. The equation for the solubility product is  $[\text{Pb}^{++}] \times [\text{SO}_4^{--}] = K_{s.p.} = [1 \times 10^{-4}] \times [1 \times 10^{-4}] = 1 \times 10^{-8}$ .

Since the product of the concentrations of the two ions can never exceed  $1 \times 10^{-8}$ , it is obvious that as the concentration of the sulfate ion in solution is increased, the concentration

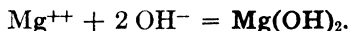
of the lead ion in solution must be reduced. If we wish to leave as little of the lead ion as possible in the solution, we must add a large excess of sulfate ions as illustrated below.

$\text{SO}_4^{--}$ (gram ions per liter)	$\text{Pb}^{++}$ (gram ions per liter)	$K_{s.p.}$
.0001 ( $1 \times 10^{-4}$ )	.0001 ( $1 \times 10^{-4}$ )	$1 \times 10^{-8}$
.001 ( $1 \times 10^{-3}$ )	.00001 ( $1 \times 10^{-5}$ )	$1 \times 10^{-8}$
.01 ( $1 \times 10^{-2}$ )	.000001 ( $1 \times 10^{-6}$ )	$1 \times 10^{-8}$

For this reason an excess of the precipitating reagent is always used in analytical chemistry. The illustration shows how we can decrease the lead ions in the solution under consideration. It is obvious that the sulfate ion concentration could be reduced in the same way by adding an excess of lead ions.

It should be noted that the solubility product rule is valid only in case the salt is relatively insoluble. Further, the common ion effect cannot be extended indefinitely. With large excess of  $\text{H}_2\text{SO}_4$ , the  $\text{PbSO}_4$  begins to dissolve and is much more soluble than in pure water. This effect may be due to the formation of a complex ion.

**The precipitation of  $\text{Mg}(\text{OH})_2$ .** When  $\text{NH}_4\text{OH}$  is added to a solution containing magnesium ions, a precipitate of  $\text{Mg}(\text{OH})_2$  is formed:



In the presence of a large excess of an ammonium salt this precipitate does not appear. This condition is explained as follows:

The ammonium hydroxide is slightly dissociated:



The addition of a large excess of an ammonium salt furnishes a large concentration of  $\text{NH}_4$  ions and, through mass action, decreases the dissociation of the  $\text{NH}_4\text{OH}$ . Therefore the concentration of  $\text{OH}$  ions becomes very small. When the  $\text{OH}^-$  ion concentration becomes so small that the product of the  $\text{Mg}^{++}$  ion concentration and the  $\text{OH}^-$  ion concentration squared is



less than the solubility product for  $\text{Mg}(\text{OH})_2$ , no precipitate of  $\text{Mg}(\text{OH})_2$  will form.

If a precipitate of  $\text{Mg}(\text{OH})_2$  has already been formed, it will dissolve when  $\text{NH}_4\text{Cl}$  is added, because the latter makes the solution unsaturated by diminishing the concentration of the  $\text{OH}$  ions.

In the same way the presence of excess of  $\text{NH}_4$  ions prevents the precipitation of  $\text{Mn}(\text{OH})_2$  and  $\text{Fe}(\text{OH})_2$ . In the case of the trivalent metals aluminum, chromium, and iron, the solubility of the hydroxides in water is so slight that the presence of ammonium salts does not prevent precipitation.

### Problems

1. The solubility of  $\text{PbSO}_4$  at  $18^\circ$  is 0.0303 gram per liter. Calculate the concentration of  $\text{PbSO}_4$  in moles per liter. *Ans.*  $1 \times 10^{-4}$ .

2. Assuming  $\text{PbSO}_4$  to be 100 per cent dissociated, calculate the concentration of lead ions and sulfate ions, in gram ions per liter, in a saturated  $\text{PbSO}_4$  solution. *Ans.*  $\text{Pb}^{++}$ :  $1 \times 10^{-4}$ .  
 $\text{SO}_4^{--}$ :  $1 \times 10^{-4}$ .

3. From the above data, calculate  $K_{sp}$  for  $\text{PbSO}_4$ . *Ans.*  $1 \times 10^{-8}$ .

4. Would a precipitate of  $\text{PbSO}_4$  be formed if 0.1 gram ion of sulfate is placed in a solution containing  $2.5 \times 10^{-8}$  gram ions of lead per liter? *Ans.* No, the product of the concentration of the ions is  $2.5 \times 10^{-9}$ .

5. How much  $\text{PbSO}_4$  would precipitate if  $5 \times 10^{-3}$  gram ions of sulfate ion is placed in a solution containing  $5 \times 10^{-3}$  gram ions of lead per liter? *Ans.*  $4.9 \times 10^{-3}$  moles.

6. After sulfate ions were added to a solution that originally contained  $8 \times 10^{-3}$  gram ions of lead ions per liter, it was found, after precipitation was complete, that 0.1 gram ion of sulfate ions remained in solution. How much  $\text{PbSO}_4$  was precipitated? *Ans.* 0.0079999 mole.

7. The solubility product of  $\text{PbCl}_2$  is  $1 \times 10^{-4}$  at  $18^\circ$ . Calculate the concentration of lead ions and chloride ions in a saturated solution of  $\text{PbCl}_2$  at  $18^\circ$ : (a) in terms of gram ions per liter; (b) in terms of grams per liter.

*Ans.* Lead, 0.02924 gram ion; 6.059 grams of lead ions. Chloride, 0.05848 gram ion; 2.075 grams of chloride ions.

8. The solubility of  $\text{CaSO}_4$  is 2 g. per liter. That of  $\text{Ag}_2\text{SO}_4$  is 8 g. per liter. Calculate the sulfate ion concentration in gram ions per liter given by each salt in its saturated aqueous solution.

*Ans.* Concentration of  $\text{SO}_4^{--}$  ions from  $\text{CaSO}_4$ :  $15 \times 10^{-3}$ .  
Concentration of  $\text{SO}_4^{--}$  ions from  $\text{Ag}_2\text{SO}_4$ :  $25 \times 10^{-3}$ .

9. The solubility of  $\text{Pb}_3(\text{PO}_4)_2$  is  $1.4 \times 10^{-4}$  g. per liter. Calculate its S.P.

Ans.  $(3 \times 1.7 \times 10^{-7})^3 \times (2 \times 1.7 \times 10^{-7})^2$ .

10. What concentration of oxalate ion must be present before any precipitate of  $\text{CaC}_2\text{O}_4$  will be formed in a saturated solution of  $\text{CaSO}_4$ ?  $K_{s.p.}$  of  $\text{CaSO}_4 = 2.3 \times 10^{-4}$ ;  $K_{s.p.}$  of  $\text{CaC}_2\text{O}_4 = 2.6 \times 10^{-9}$ .

Ans.  $1.7 \times 10^{-7}$  gram ions per liter.

### NOTE

For a more extensive list of problems relating to percentage strengths of solution, molarity, normality, chemical equilibrium, ionization and solubility products the student is referred to the following problem books:

Engelder, C. J., *Calculations of Qualitative Analysis*. Wiley, New York, 1942.

Schaum, D., *Theory and Problems*. Schaum, New York, 1949.

Sorum, C. H., *Problems for General Chemistry and Qualitative Analysis*. Banta, Menasha, Wis., 1949.

## COLLOIDS IN QUALITATIVE ANALYSIS

Many of the precipitates formed during the operations of qualitative analysis consist of fine particles showing all the properties of substances in the colloidal state. They may be peptized and coagulated, and they adsorb electrolytes from solution. The precipitates are often so finely divided that they do not settle when centrifuged, and they cannot be removed by filtration because the particles are so small that they pass through the pores of the filter paper. The substances that cause the most trouble in this respect are hydroxides and sulfides of the metals and occasionally elementary sulfur.

**Coagulation.** Since such colloidal suspensions are composed of small electrically charged particles, they are precipitated by electrolytes. The precipitating reagents used in qualitative analysis are either acids, bases, or salts; consequently, the excess of the precipitant helps coagulate the precipitate. In certain cases, as in the precipitation of the aluminum-nickel group, the presence of a strong electrolyte ( $\text{NH}_4\text{Cl}$ ) helps assure coagulation of the precipitate.

**Washing precipitates.** Cold water tends to peptize certain colloidal substances, the sulfides being especially susceptible. To avoid peptizing, hot wash water may be used; also the wash water may contain a small amount of  $\text{NH}_4\text{NO}_3$  or some other electrolyte.

**Occlusion.** Because of the large surface possessed by amorphous precipitates, appreciable amounts of soluble electrolytes are adsorbed when precipitates of this kind are formed. This adsorption, or occlusion as it is called, complicates the separation of metallic ions. Among the gelatinous precipitates the behavior of  $\text{Fe}(\text{OH})_3$  is typical; it shows this tendency to a marked extent, so that thorough washing of this and similar precipitates is absolutely necessary. The effect of occlusion is further illustrated by the fact that cadmium sulfide occludes chloride, sulfate, and other ions to so great an extent that a solubility product for  $\text{CdS}$  has no value.

### References

For detailed discussions on the theories and practice of qualitative analysis, the student is referred to the following texts:

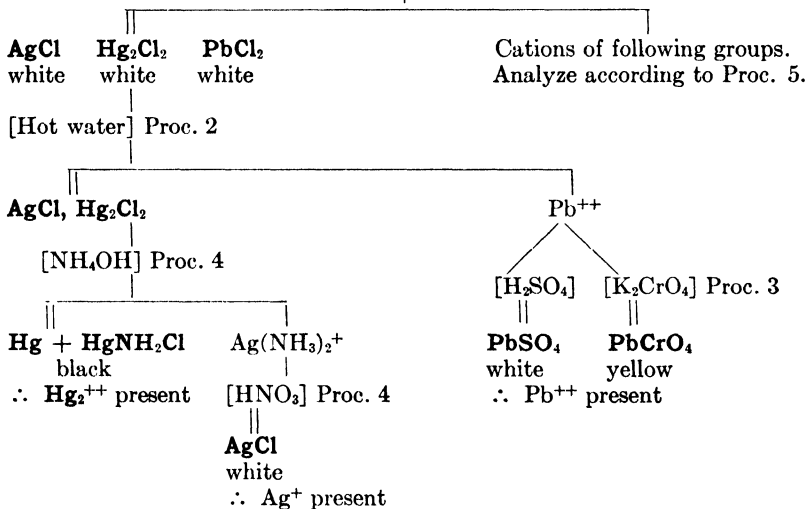
- Curtman, L. J., *Introduction to Semimicro Qualitative Analysis*. Macmillan, New York, 1947.
- , *Qualitative Chemical Analysis*. Macmillan, New York, 1935.
- , and Edmonds, S. M., *Calculations of Qualitative Analysis*. Macmillan, New York, 1940.
- Hogness, T. R., and Johnson, W. C., *Qualitative Analysis and Chemical Equilibrium*. Holt, New York, 1940.
- Meldrum, W. B., and Daggett, A. F., *A Textbook of Qualitative Analysis*. American Book, New York, 1946.
- Noyes, A. A. and Bray, W. C., *A System of Qualitative Analysis for the Rare Elements*. Macmillan, New York, 1927.
- , and Swift, E. H., *Qualitative Chemical Analysis*. Macmillan, New York, 1942.
- Prescott, A. B., and Johnson, O. C., *Qualitative Chemical Analysis* (rewritten by McAlpine and Soule). Van Nostrand, New York, 1933.
- Reedy, J. H., *Theoretical Qualitative Analysis*. McGraw-Hill, New York, 1938.
- Treadwell, E. P., and Hall, W. T., *Analytical Chemistry*, Vol. I. Wiley, New York, 1937.

## CHAPTER 3

### The Silver Group

Solution containing  $\text{Ag}^+$ ,  $\text{Hg}_2^{++}$ ,  $\text{Pb}^{++}$ ,  $\text{Hg}^{++}$ ,  $\text{Bi}^{+++}$ ,  $\text{Cu}^{++}$ ,  $\text{Cd}^{++}$ ,  $\text{Sn}^{++++}$ ,  $\text{As}^{+++}$ ,  $\text{Sb}^{+++}$ ,  $\text{Al}^{+++}$ ,  $\text{Cr}^{+++}$ ,  $\text{Fe}^{++}$ ,  $\text{Fe}^{+++}$ ,  $\text{Mn}^{++}$ ,  $\text{Zn}^{++}$ ,  $\text{Ni}^{++}$ ,  $\text{Co}^{++}$ ,  $\text{Ba}^{++}$ ,  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{H}_2\text{AsO}_3^-$  and  $\text{AsO}_4^{--}$ .

[Cold 6N HCl] Proc. 1.



#### OUTLINE 2: ANALYSIS OF THE SILVER GROUP

### PRECIPITATION AND ANALYSIS OF THE SILVER GROUP

The chlorides of silver, mercury I, and lead are insoluble in cold water and cold dilute hydrochloric acid; the chlorides of all other metals are soluble. (See Solubility Rule 3, page 170.) This fact is the basis for the separation of silver, mercury I, and lead from all other metallic ions.

When HCl or some other soluble chloride is added to a solu-

tion containing all of the common cations,  $\text{AgCl}$ ,  $\text{Hg}_2\text{Cl}_2$ , and  $\text{PbCl}_2$  are precipitated. All other metals remain in solution as soluble chlorides (see Outline 2). The ions of silver, mercury I, and lead constitute the silver group. Since  $\text{HCl}$  is used to separate this group of ions from other cations by precipitating them as insoluble chlorides, it is called the *group reagent* for the silver group.

### Procedure 1: Precipitation of the silver group

Place 5 drops of the solution to be analyzed in a 3-in. test tube and add 5 drops of water (see Note 1). Add 2 drops of 6N  $\text{HCl}$  and mix thoroughly by stirring the contents of the test tube with a glass stirring rod. With a few drops of cold water, wash down into the solution any precipitate which adheres to the inside of the test tube above the level of the solution (see Note 2). Centrifuge (see Note 3). Test for complete precipitation by adding another drop of 6N  $\text{HCl}$  to the clear supernatant solution in the test tube (see Note 4). When precipitation is complete, centrifuge (see Note 5) and then decant (see Note 6). Save the decantate, which contains the cations of the following groups, for Procedure 5 (see Note 7). Wash the precipitate twice with 10-drop portions of cold water (see Note 8), adding the washings to the decantate being saved for Procedure 5. Allow the precipitate to remain in the test tube and analyze it according to Procedure 2 (see Note 9).

### NOTES

1. The dropwise addition of water, solutions, or liquid reagents is done with a medicine dropper. All liquid-reagent bottles are fitted with medicine droppers. Each student's desk will be provided with several medicine droppers.

2. In the present system of semimicro analytical procedures, solid precipitates are separated from liquids by centrifuging and decantation rather than by filtration. The centrifugal force imparted by the whirling centrifuge causes the heavy precipitate to be thrown to the bottom of the tube, the lighter liquid remaining on top. Any precipi-

tate that happens to be clinging to the sides of the tube above the level of the liquid will remain there and will not be thrown down with the rest of the precipitate. Its presence on the walls of the tube will interfere with subsequent decantation. Therefore, any precipitate adhering to the inside walls of the test tube should always be washed down with a few drops of water or other appropriate reagent before the solution is centrifuged.

3. The test tube containing the material to be centrifuged must always be balanced in the centrifuge by a test tube containing an equal amount of water or other solution.

4. In all future procedures in which precipitation is used to accomplish a separation of substances, it shall be understood that a test for complete precipitation must always be made. If the test shows that precipitation is not complete, add some more of the precipitating reagent, mix thoroughly by stirring the contents of the test tube with a glass stirring rod, and then centrifuge.

5. The length of centrifuging time required will depend upon the nature of the precipitate. Most precipitates require only 15 to 30 seconds of centrifuging; however, some very finely divided precipitates may require several minutes. Proper centrifuging should give a clear supernatant liquid, with the precipitate packed into the bottom of the tube. If the supernatant liquid is not clear, more centrifuging is required.

6. As a result of settling by centrifuging, most precipitates are so well packed into the bottom of the test tube that the supernatant liquid can be decanted (poured off) without much danger of disturbing the precipitate. The last drop of decantate can even be removed from the lip of the test tube by gentle tapping. Some precipitates, however, are so light and fluffy that decantation of the supernatant liquid can be accomplished only with great care, and even then a part of the supernatant liquid must be allowed to remain behind with the precipitate. In a few instances, to be noted in later procedures, the precipitate is so light that decantation cannot be accomplished even with the exercise of great care; in such instances the top 75–80 per cent of the supernatant liquid is drawn off with a medicine dropper fitted with a long, finely pointed tube. If the decantate is to be discarded, as in a washing operation, the loss of bits of precipitate in the decantate is of no consequence. If, however, the decantate is to be submitted to further analysis it must not contain any precipitate; if precipitate does get into the decantate the process of centrifuging and decantation must be repeated. Because the 3-in. test tubes are of such small diameter ( $\frac{3}{8}$  in.), surface tension may cause the failure of decantates to flow out over the lip of the tilted tube. If the lip of

another test tube or the end of a stirring rod is touched to the solution at the lip of the tube, the decantate will flow out.

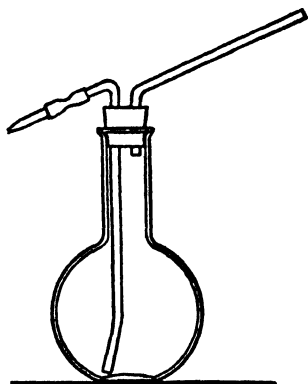
7. If the solution being analyzed is known to contain only cations of the silver group (see Schedule of Laboratory Work, 1 and 2, page 6), this decantate may be discarded.

8. Wash a precipitate as follows: add the water or other washing liquid to the precipitate in the test tube, mix thoroughly by stirring the contents of the tube with a glass stirring rod, centrifuge, and decant. *Failure to wash precipitates thoroughly is one of the main sources of error in qualitative analysis.*

9. If a precipitate or solution is to be preserved from one laboratory period to the next, the test tube in which it is kept should be stoppered. Stoppering prevents contamination and also keeps solutions from evaporating and precipitates from drying out. Test tubes should be labeled so that their contents can be correctly identified.

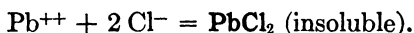
10. If no precipitate is formed with cold  $\text{HCl}$ , the absence of the ions of silver and mercury I is definitely proved. However, lead may be present in small quantities, since  $\text{PbCl}_2$  is appreciably soluble even in cold water.

11. The object of the silver-group precipitation is to remove from solution, as completely as possible, the  $\text{Ag}^+$ ,  $\text{Hg}_2^{++}$ , and  $\text{Pb}^{++}$  ions by precipitating them as  $\text{AgCl}$ ,  $\text{Hg}_2\text{Cl}_2$ , and  $\text{PbCl}_2$ . A precipitate will form when the product of the concentration of the ions that react to form the precipitate just exceeds the solubility product (see page 27). Furthermore, in any precipitation process the insoluble compound will keep precipitating until the concentrations of its ions remaining in solution reach values at which their product just equals the solubility product. It follows, therefore, that an excess of the group reagent ion,  $\text{Cl}^-$  in this case, is desirable, since if the concentration of  $\text{Cl}^-$  is high, the concentration of  $\text{Ag}^+$ ,  $\text{Hg}_2^{++}$ , and  $\text{Pb}^{++}$  remaining in solution will be low. An inordinately large excess of the reagent may, however, change the nature of the solution completely or may form soluble complex compounds, thus nullifying the usual advantage resulting from having an excess of reagent. A very large excess of  $\text{HCl}$  will actually increase the amount of lead remaining in solution because of the formation of the soluble complex compound  $\text{H}_2\text{PbCl}_4$ .



Wash Bottle.

12. Other soluble chlorides such as  $\text{NH}_4\text{Cl}$  could be substituted for  $\text{HCl}$ , since the reaction is one between ions:



13. It is desirable for each student to have a wash bottle of the type illustrated in the figure on page 39. The capacity should be about 150 ml.; either a Florence flask or an Erlenmeyer flask may be used.

## SEPARATION OF LEAD FROM SILVER AND MERCURY I

The silver-group precipitate is a mixture of  $\text{PbCl}_2$ ,  $\text{Hg}_2\text{Cl}_2$ , and  $\text{AgCl}$ . It is necessary to separate each individual member of the group in order that its presence may be confirmed. Lead is separated first.  $\text{PbCl}_2$  is soluble in hot water;  $\text{AgCl}$  and  $\text{Hg}_2\text{Cl}_2$  are insoluble. This difference is the basis for the separation of lead ions from mercury I and silver ions.

### Procedure 2: Separation of lead from silver and mercury I

Add 15–20 drops of hot water (see Note 1) to the test tube containing the precipitate from Procedure 1 and heat to boiling (see Note 2). Centrifuge at once and decant into another test tube immediately after centrifuging; save the decantate, which contains  $\text{Pb}^{++}$ , for Procedure 3. Wash the precipitate twice with 10-drop portions of hot water (see Note 3) and save it, in the test tube, for Procedure 4.

### NOTES

1. A beaker or flask of hot distilled water should always be available on the desk. A medicine dropper to be used exclusively for hot water should be kept in this beaker or flask. A second beaker or flask and medicine dropper should be provided for cold distilled water. Additional medicine droppers should be available for transferring solutions. The use of one dropper for all operations is liable to result in contamination. Since avoidance of contamination is imperative if good results are to be obtained, it is important that test tubes, casserole, stirring rods, medicine droppers, and similar pieces of equipment be cleaned with tap water and rinsed with distilled water



*directly after they have been used* and before they are put down on the desk. If this rule is followed, every piece of equipment will be clean. The practice of placing a clean towel, folded to approximately a 12-in. square, on the desk top during the laboratory period and keeping test tubes, stirring rods, extra medicine droppers, test-tube brush, and casseroles on this towel is highly recommended.

2. Great care must be taken when a liquid is boiled in a small test tube; otherwise it may be thrown completely out of the tube. Hold the tube well above the flame with a test-tube holder and move it back and forth in such a manner that the top as well as the bottom of the liquid in the tube is heated. Solutions that "bump" badly when boiled should be heated in a casserole.

3. Unless specified otherwise washings are always discarded.

4. 100 cc. of water at 0°C. dissolves 0.673 g. of  $\text{PbCl}_2$ . 100 cc. of water at 100°C. dissolves 3.34 g. of  $\text{PbCl}_2$ .

5. Since  $\text{PbCl}_2$  is appreciably soluble in cold dilute  $\text{HCl}$ , lead will not be completely precipitated in the silver group. The lead ions remaining in solution will be completely precipitated as lead sulfide in the next group, the copper-arsenic group.

### Procedure 3: Detection of lead

Cool the decantate from Procedure 2 and divide into two parts. To one part add 1 drop of  $\text{NK}_2\text{CrO}_4$  solution; a yellow precipitate ( $\text{PbCrO}_4$ ) proves the presence of lead. To the second part add 1 drop of 4N  $\text{H}_2\text{SO}_4$ ; a white precipitate ( $\text{PbSO}_4$ ), which may form slowly, is further proof of the presence of lead.

#### NOTE

100 cc. of water at 20°C. dissolves 0.003 g. of  $\text{PbSO}_4$ . 100 cc. of water at 20°C. dissolves 0.000007 g. of  $\text{PbCrO}_4$ . Obviously,  $\text{PbCrO}_4$  provides a much more sensitive test for lead than does  $\text{PbSO}_4$ . Substances which dissolve to such a limited extent as  $\text{PbCrO}_4$  and  $\text{PbSO}_4$  are called *insoluble*.

## SEPARATION AND DETECTION OF SILVER AND MERCURY

$\text{AgCl}$  is soluble in  $\text{NH}_4\text{OH}$ .  $\text{Hg}_2\text{Cl}_2$  reacts with  $\text{NH}_4\text{OH}$  to form  $\text{Hg}$  and  $\text{HgNH}_2\text{Cl}$ , both insoluble. This fact is the basis for the separation of silver ions from mercury I ions.

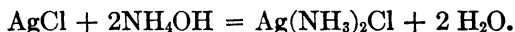
**Procedure 4: Separation and detection of mercury I and silver**

Add 10 drops of 15N  $\text{NH}_4\text{OH}$  to the precipitate from Procedure 2, mix thoroughly, centrifuge, and decant into another test tube, saving the decantate for testing for silver. A black residue ( $\text{Hg} + \text{HgNH}_2\text{Cl}$ ) proves the presence of mercury I. To the decantate add 16N  $\text{HNO}_3$ , drop by drop, with constant mixing with a stirring rod, until slightly acid (see Note 1). A white precipitate ( $\text{AgCl}$ ) proves the presence of silver.

**NOTES**

1. Test for the acidity or alkalinity of a solution as follows: Place a piece of litmus paper on the clean towel or drape it over the edge of a beaker. Withdraw the stirring rod used for stirring the solution and touch the end of it to the piece of litmus paper.

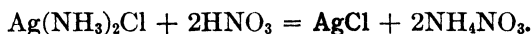
2.  $\text{AgCl}$  dissolves in  $\text{NH}_4\text{OH}$  as follows:



This complex salt ionizes as follows:



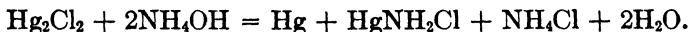
3. When the complex salt  $\text{Ag}(\text{NH}_3)_2\text{Cl}$  is treated with an acid, it is decomposed with the formation of insoluble  $\text{AgCl}$ :



4. The formation of the complex ion,  $\text{Ag}(\text{NH}_3)_2^+$ , is an example of a type of reaction that will be encountered in connection with the detection of other metallic ions. Similar complexes are  $\text{Cu}(\text{NH}_3)_4^{++}$ ,  $\text{Ni}(\text{NH}_3)_4^{++}$ ,  $\text{Co}(\text{NH}_3)_6^{++}$ ,  $\text{Zn}(\text{NH}_3)_4^{++}$ , and  $\text{Cd}(\text{NH}_3)_4^{++}$ . The complex ion of silver is the silver diammine ion, also called the silver ammonia ion. The compounds which furnish these ions are called *ammines*.  $\text{Ag}(\text{NH}_3)_2\text{Cl}$  is silver diammine chloride.

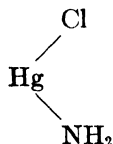
5. If the  $\text{PbCl}_2$  is not completely removed from the precipitate of  $\text{AgCl}$  and  $\text{Hg}_2\text{Cl}_2$ , it is converted by the  $\text{NH}_4\text{OH}$  into the finely divided insoluble basic salt,  $\text{Pb}(\text{OH})\text{Cl}$ , which may give a turbid decantate. The basic salt will dissolve in  $\text{HNO}_3$  and will not interfere with the confirmatory test for silver.

6.  $\text{NH}_4\text{OH}$  reacts with  $\text{Hg}_2\text{Cl}_2$  to produce a mixture of black finely divided mercury ( $\text{Hg}$ ) and white mercuric amino chloride ( $\text{HgNH}_2\text{Cl}$ ) according to the equation



The compound  $\text{HgNH}_2\text{Cl}$  may be considered as a derivative of  $\text{HgCl}_2$  in which the amino group ( $\text{NH}_2$ ) has replaced one atom of chlorine,

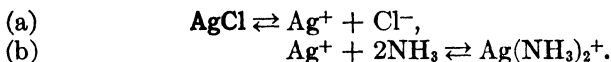
thus:



7. Mercury I exists in solution as the stable diatomic ion,  $\text{Hg}_2^{++}$ . Therefore the precipitate of mercury I chloride is  $\text{Hg}_2\text{Cl}_2$  rather than  $\text{HgCl}$ .

8. The dissolving of  $\text{AgCl}$  by  $\text{NH}_4\text{OH}$  and the failure of  $\text{AgCl}$  to be dissolved by  $\text{HNO}_3$  may be interpreted in terms of the following general rule: When a water-insoluble electrolyte is dissolved, at least two reactions will always be set up. One of these reactions, called (a), will be an equilibrium between the insoluble electrolyte and its ions. The second reaction, called (b), will be between one of the ions in (a) and some substance (either an ion or a molecule) with which this ion reacts to form a new stable substance or substances, either a new ion or a new molecule. The two reactions (a) and (b) have one ion in common. If the concentration of the common ion in reaction (b) is less than the concentration of this same ion necessary to maintain equilibrium (a), the insoluble electrolyte will dissolve. If the concentration of the common ion in reaction (b) is greater than the concentration of this same ion in equilibrium (a), or if no reaction (b) is set up, the precipitate will not dissolve.

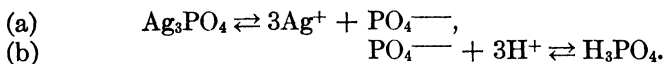
The rule will apply to the dissolving of  $\text{AgCl}$  by  $\text{NH}_3$  as follows:



$\text{Ag}(\text{NH}_3)_2^+$  is a very stable ion; therefore the equilibrium point in (b) is far to the right and the concentration of the  $\text{Ag}^+$  in this equilibrium will be low. If it is lower than the concentration of  $\text{Ag}^+$  required for (a), more  $\text{AgCl}$  will go into solution in an effort to build up the concentration of  $\text{Ag}^+$  to the value required for (a). An excess of  $\text{NH}_3$  will shift equilibrium (b) far to the right, thereby keeping the concentration of  $\text{Ag}^+$  so low that the  $\text{AgCl}$  will eventually all go into solution.

$\text{AgCl}$  will not dissolve in  $\text{HNO}_3$ . Equilibrium (a) exists as noted above. No reaction (b) is set up because neither  $\text{Ag}^+$  nor  $\text{Cl}^-$  will react with either  $\text{H}^+$  or  $\text{NO}_3^-$  to form a stable substance.

To develop this concept further, consider the fact that  $\text{Ag}_3\text{PO}_4$  will dissolve in  $\text{HNO}_3$ :

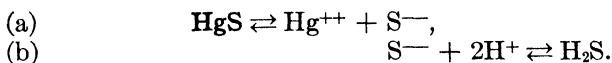


In this instance  $\text{PO}_4^{3-}$  is the common ion; it combines with the hydrogen ions from the strong acid  $\text{HNO}_3$  to form the weak acid  $\text{H}_3\text{PO}_4$ . If the concentration of hydrogen ions in (b) is kept high, the concentration of  $\text{PO}_4^{3-}$  ions will be kept so low that the  $\text{Ag}_3\text{PO}_4$  will dissolve eventually.

$\text{Ag}_3\text{PO}_4$  will not dissolve in  $\text{HC}_2\text{H}_3\text{O}_2$  because the latter, being a weak acid, provides so few  $\text{H}^+$  ions that the equilibrium point in (b) is not shifted far enough to the right to bring the concentration of  $\text{PO}_4^{3-}$  in (b) below the concentration of  $\text{PO}_4^{3-}$  in (a).

In general, and in accordance with the above interpretation, water-insoluble salts of strong acids are insoluble in either strong or weak acids. Water-insoluble salts of weak acids are soluble in strong acids but insoluble in weak acids.

If the salt of a weak acid is extremely insoluble in water it may not be soluble in a strong acid.  $\text{HgS}$  is insoluble in  $\text{HCl}$  even though it is the salt of the weak acid  $\text{H}_2\text{S}$ .

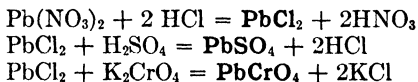


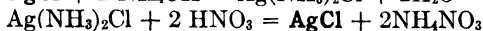
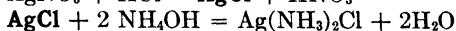
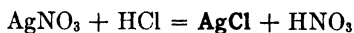
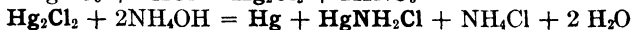
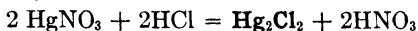
$\text{HgS}$  is so insoluble that the concentration of  $\text{S}^{--}$  in (a) is so low that the concentration of  $\text{S}^{--}$  in (b) cannot be made lower, not even with a high concentration of  $\text{H}^+$ .

The two-reaction rule noted above can be applied without any great difficulty to the dissolving of most precipitates. The stable substance formed in equation (b) may be water, a weak acid, a complex ion, or an un-ionized substance. In certain cases, as when a sulfide is dissolved by moderately concentrated  $\text{HNO}_3$ , equation (b) may be a complete reaction in which an ion is oxidized to the free element (see Note 5, Procedure 7). The detailed discussion of the application of the above rule to each case in which a precipitate is dissolved will, in general, not be presented. However, the student is expected to be able to apply the rule in every case.

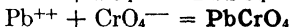
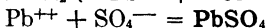
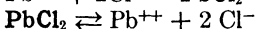
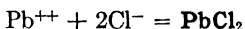
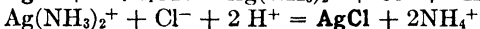
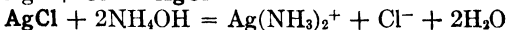
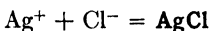
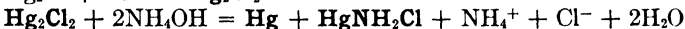
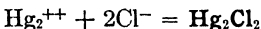
#### MOLECULAR EQUATIONS

##### Lead



*Silver**Mercury*

## IONIC EQUATIONS

*Lead**Silver**Mercury*

## Questions

1. Using the scheme of analysis as a guide, write equations for all reactions that take place in the precipitation and analysis of the silver group.
2. You are asked to make up a water solution of an unknown which will contain lead, silver, mercury I, copper, manganese, barium, and sodium ions, all in the same solution. What salt (examples: sulfate, nitrate, carbonate, acetate, chloride) of each of the metals would you use to obtain a clear solution containing all seven of the above ions?
3. What reagents could be used in place of HCl as the group reagent for the silver group?
4. Cold dilute  $\text{H}_2\text{SO}_4$  was accidentally used in place of cold concentrated HCl as the group reagent for the silver group in the analysis of an unknown solution. A white precipitate formed. Explain.
5. A solution of  $\text{Na}_2\text{CO}_3$  in water was accidentally used in place of HCl as the group reagent for the silver group in the analysis of an unknown solution. A heavy precipitate formed. Explain.
6. State the fact upon which each of the following is based:
  - a. The separation of silver, lead, and mercury I ions from all other cations.

- b. The separation of lead ions from silver and mercury I ions.
- c. The separation of silver ions from mercury I ions.
- d. The confirmatory tests for lead, silver, and mercury I (ous) ions.

7. In the analysis of an unknown solution, what difficulty, if any, would arise if:

- a. Hot concentrated HCl were used instead of cold HCl in the precipitation of the silver group.
- b. The precipitate of AgCl and Hg<sub>2</sub>Cl<sub>2</sub> were not washed free from PbCl<sub>2</sub>.
- c. The silver-group precipitate (AgCl, Hg<sub>2</sub>Cl<sub>2</sub> and PbCl<sub>2</sub>) were washed too long with cold water.
- d. A large excess of concentrated HCl were used in the silver-group precipitation.
- e. Not enough HNO<sub>3</sub> were added in the confirmatory test for silver.

8. Give the formula for a chemical substance which will:

- a. Form a precipitate with KCl solution and also with CuCl<sub>2</sub>.
- b. Form a precipitate with HCl and also with H<sub>2</sub>SO<sub>4</sub>.
- c. Form a precipitate with NH<sub>4</sub>Cl solution and also with K<sub>2</sub>CrO<sub>4</sub>.
- d. Form a precipitate with HCl and also with HNO<sub>3</sub>.
- e. Form a precipitate with HCl but not with HNO<sub>3</sub>.
- f. Form a precipitate with AgNO<sub>3</sub> solution but not with Bi(NO<sub>3</sub>)<sub>3</sub>.
- g. Form a precipitate with HgNO<sub>3</sub> solution but not with Hg(NO<sub>3</sub>)<sub>2</sub>.
- h. Form a precipitate with Ag(NH<sub>3</sub>)<sub>2</sub>Cl solution but not with AgNO<sub>3</sub>.
- i. Readily dissolve PbCl<sub>2</sub> but not AgCl.
- j. Readily dissolve CuCl<sub>2</sub> but not PbCl<sub>2</sub>.
- k. Readily dissolve AgCl but not Hg<sub>2</sub>Cl<sub>2</sub>.
- l. Readily dissolve HgCl<sub>2</sub> but not Hg<sub>2</sub>Cl<sub>2</sub>.
- m. Readily dissolve Pb(NO<sub>3</sub>)<sub>2</sub> but not PbSO<sub>4</sub>.
- n. Form a precipitate with Na<sub>2</sub>CrO<sub>4</sub> but not with NaNO<sub>3</sub>.

9. By means of what single reagent could you distinguish between the following? (Tell what happens to each substance.)

a. *Solutions:*

AgNO <sub>3</sub> and Zn(NO <sub>3</sub> ) <sub>2</sub> .	H <sub>2</sub> SO <sub>4</sub> and HCl.
K <sub>2</sub> CrO <sub>4</sub> and KNO <sub>3</sub> .	H <sub>2</sub> SO <sub>4</sub> and HNO <sub>3</sub> .
HCl and HNO <sub>3</sub> .	Hg(NO <sub>3</sub> ) <sub>2</sub> and HgNO <sub>3</sub> .
Pb(NO <sub>3</sub> ) <sub>2</sub> and Hg(NO <sub>3</sub> ) <sub>2</sub> .	Ag(NH <sub>3</sub> ) <sub>2</sub> Cl and AgNO <sub>3</sub> .

b. *Solids:*

Hg <sub>2</sub> Cl <sub>2</sub> and HgCl <sub>2</sub> .	AgCl and CdCl <sub>2</sub> .
PbCl <sub>2</sub> and Hg <sub>2</sub> Cl <sub>2</sub> .	AgCl and Hg <sub>2</sub> Cl <sub>2</sub> .
PbSO <sub>4</sub> and Pb(NO <sub>3</sub> ) <sub>2</sub> .	PbCrO <sub>4</sub> and K <sub>2</sub> CrO <sub>4</sub> .

10. An unknown solution, which was known to contain only cations of the silver group, gave no precipitate when heated to boiling and treated with hot concentrated HCl but gave a white precipitate when cooled and treated with cold concentrated HCl. What conclusions can be drawn?

**11.** In the analysis of an unknown solution which was known to contain only cations of the silver group, the white precipitate obtained by adding cold HCl to the unknown solution partly dissolved in hot water. The residue dissolved completely in  $\text{NH}_4\text{OH}$ . What cations were present? Absent?

**12.** The white precipitate obtained when cold HCl was added to an unknown solution was completely insoluble in both hot water and  $\text{NH}_4\text{OH}$ . What conclusions can be drawn?

**13.** The white precipitate obtained when cold HCl was added to an unknown solution was completely insoluble in hot water and completely soluble in  $\text{NH}_4\text{OH}$ . What conclusions can be drawn?

## **Silver-group report**



## Silver-group report

## **Silver-group report**

## **Silver-group report**

Solution containing  $\text{Pb}^{++}$ ,  $\text{Hg}^{++}$ ,  $\text{Bi}^{+++}$ ,  $\text{Cu}^{++}$ ,  $\text{Cd}^{++}$ ,  $\text{Sn}^{++}$ ,  $\text{As}^{+++}$ ,  $\text{Sb}^{+++}$ ,  $\text{Al}^{+++}$ ,  $\text{Cr}^{+++}$ ,  $\text{Fe}^{++}$ ,  $\text{Fe}^{+++}$ ,  $\text{Mn}^{++}$ ,  $\text{Zn}^{++}$ ,  $\text{Ni}^{++}$ ,  $\text{Co}^{++}$ ,  $\text{Ca}^{++}$ ,  $\text{Ba}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{K}^{+}$ ,  $\text{Na}^{+}$  and  $\text{NH}_4^{+}$

[HCl,  $\text{H}_2\text{S}$ ] Proc. 5

Cations of following groups.  
Analyze according to Proc. 15

$\text{HgS}$ ,  $\text{PbS}$ ,  $\text{Bi}_2\text{S}_3$ ,  $\text{CuS}$ ,  $\text{SnS}$ ,  $\text{CdS}$ ,  $\text{SnS}$ ,  $\text{As}_2\text{S}_3$ ,  $\text{AsS}_4$ ,  $\text{Sb}_2\text{S}_3$

[( $\text{NH}_4$ ) $_2\text{S}$ ] Proc. 6

$\text{HgS}$ ,  $\text{PbS}$ ,  $\text{Bi}_2\text{S}_3$ ,  $\text{CuS}$ ,  $\text{CdS}$   
[ $\text{HNO}_3$ ] Proc. 7

$\text{HgCl}_2$   
[ $\text{SnCl}_2$ ]  
 $\text{Hg} + \text{Hg}_2\text{Cl}_2$   
gray  
 $\therefore \text{Hg}^{++}$  present

$\text{Pb}^{++}$ ,  $\text{Bi}^{+++}$ ,  $\text{Cu}^{++}$ ,  $\text{Cd}^{++}$   
[ $\text{H}_2\text{SO}_4$ ] Proc. 8

$\text{PbSO}_4$   
white  
[ $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ ]  
 $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$   
[ $\text{K}_2\text{C}_2\text{O}_4$ ]  
 $\text{PbC}_2\text{O}_4$   
yellow  
 $\therefore \text{Pb}^{++}$  present

$\text{Bi}^{+++}$ ,  $\text{Cu}^{++}$ ,  $\text{Cd}^{++}$   
[ $\text{NH}_4\text{OH}$ ] Proc. 9

$\text{Bi}(\text{OH})_3$   
[ $\text{Na}_2\text{SnO}_3$ ]  
 $\text{Bi}$   
black  
 $\therefore \text{Bi}^{+++}$  present

$\text{Cu}(\text{NH}_3)_4^{++}$ ,  $\text{Cd}(\text{NH}_3)_4^{++}$   
[ $\text{H}_2\text{O}_2$ ]  
 $\text{Cu}^{++}$ ,  $\text{Cd}^{++}$   
[ $\text{K}_2\text{Fe}(\text{CN})_6$ ]  
 $\text{CuFe}(\text{CN})_6$   
red  
 $\therefore \text{Cu}^{++}$  present

[ $\text{KCN}$ ,  $\text{H}_2\text{S}$ ]  
 $\text{CdS}$   
yellow  
 $\therefore \text{Cd}^{++}$  present

[ $\text{H}_2\text{C}_2\text{H}_3\text{O}_2$ ]  
 $\text{Cu}^{++}$ ,  $\text{Cd}^{++}$   
[ $\text{K}_2\text{Fe}(\text{CN})_6$ ]  
 $\text{CuFe}(\text{CN})_6$   
red  
 $\therefore \text{Cu}^{++}$  present

[ $\text{H}_2\text{C}_2\text{H}_3\text{O}_2$ ]  
 $\text{Cu}^{++}$ ,  $\text{Cd}^{++}$   
[ $\text{K}_2\text{Fe}(\text{CN})_6$ ]  
 $\text{CuFe}(\text{CN})_6$   
red  
 $\therefore \text{Cu}^{++}$  present

[ $\text{H}_2\text{C}_2\text{H}_3\text{O}_2$ ]  
 $\text{Cu}^{++}$ ,  $\text{Cd}^{++}$   
[ $\text{K}_2\text{Fe}(\text{CN})_6$ ]  
 $\text{CuFe}(\text{CN})_6$   
red  
 $\therefore \text{Cu}^{++}$  present

$\text{Cu}^{++}$ ,  $\text{Cd}^{++}$   
[ $\text{K}_2\text{Fe}(\text{CN})_6$ ]  
 $\text{CuFe}(\text{CN})_6$   
red  
 $\therefore \text{Cu}^{++}$  present

$\text{Cu}^{++}$ ,  $\text{Cd}^{++}$   
[ $\text{K}_2\text{Fe}(\text{CN})_6$ ]  
 $\text{CuFe}(\text{CN})_6$   
red  
 $\therefore \text{Cu}^{++}$  present

OUTLINE 3: THE ANALYSIS OF THE COPPER-ARSENIC GROUP

## CHAPTER 4

### The Copper-Arsenic Group

THE SULFIDES of lead, mercury II, bismuth, copper, cadmium, arsenic, antimony, and tin are insoluble in dilute HCl. The sulfides of all metals of the following groups are soluble in HCl. Upon this fact is based the separation of the cations of the copper-arsenic group from the cations of the following groups.

#### Procedure 5: Precipitation of the copper-arsenic group

If the solution to be analyzed is a copper-arsenic group "known" or "unknown" containing only cations of the copper-arsenic group (see Schedule of Laboratory work 3 and 4, page 6), then follow Part (A). If the decantate from Procedure 1 of the silver-group precipitation is to be analyzed, follow (B).

(A) Place 6 drops of the solution to be analyzed in a casserole and add 6 drops of 6N HCl. Evaporate the solution in the casserole down to a pasty mass (see Note 1), being very careful not to bake the residue. Cool, and then proceed as directed in (C) below.

(B) Place the decantate from Procedure 1 in a casserole, add 6 drops of 6N HCl and evaporate carefully down to a pasty mass (see Note 1), cool, and proceed as directed in (C) below.

(C) To the residue in the cool casserole add exactly 6 drops of 12N HCl. Swish the acid around until all of the residue is dissolved; if necessary stir the mixture and warm slightly. Transfer the solution to a 3-in. test tube, heat carefully until it begins to show signs of effervescence, then treat with  $\text{H}_2\text{S}$  for 10–20 seconds (see Note 2). Dilute with 10 drops of hot water and treat with  $\text{H}_2\text{S}$  for another 10–20 seconds. Dilute

with 10 drops of cold water and treat with  $\text{H}_2\text{S}$  for 10–20 more seconds, being sure that the  $\text{H}_2\text{S}$  gas is bubbled all the way to the bottom of the solution. Finally, add 15 more drops of cold water and treat with  $\text{H}_2\text{S}$  for another 10–20 seconds. When precipitation is complete, wash down with water any precipitate on the walls of the test tube, centrifuge, and decant. Boil the decantate, which contains the cations of the following groups, for 1 minute and save it for Procedure 15 (see Note 3). Wash the precipitate twice with 15-drop portions of hot water and analyze according to Procedure 6.

#### NOTES

1. Evaporate the solution in the casserole as follows: Hold the casserole in your hand and pass it back and forth over the top of the flame. At the end of every two or three back-and-forth passes tilt the casserole slightly so that the solution will run to its lower edge. In the course of the back-and-forth pass the solution is swished around over the bottom of the casserole. Be very careful not to overheat to the point where the residue begins to bake. If brown areas develop on the bottom of the casserole, indicating baking, swish the remaining solution around until the brown area is removed. When only two or three drops of liquid remain, remove from above the flame and let the heat of the casserole complete the evaporation. Baking the residue must be avoided; baking may sublime off the chlorides of arsenic, mercury, and tin.

2. A solution is treated with  $\text{H}_2\text{S}$  as follows: Attach to the rubber outlet tube at the source of  $\text{H}_2\text{S}$  a clean glass bubbling tube. This bubbling tube is made by drawing down a glass tube of suitable diameter to a fairly fine constricted end. The over-all length of the bubbling tube should be about 5 in. Insert the end of the bubbling tube to within  $\frac{1}{4}$  in. of the surface of the solution in the test tube, open the  $\text{H}_2\text{S}$  outlet valve, and then gradually bring the constricted tip of the bubbling tube down to the bottom of the solution. The constricted tube will deliver a stream of very fine bubbles; large bubbles would tend to throw the solution out of the small test tube. If the tip of the bubbling tube is brought all the way to the bottom of the solution before the  $\text{H}_2\text{S}$  gas is turned on, the sudden rush of gas when the  $\text{H}_2\text{S}$  valve is opened may throw the solution out of the test tube. A very rapid rate of  $\text{H}_2\text{S}$  bubbling should be avoided.

If the source of  $\text{H}_2\text{S}$  is a Kipp generator or other portable generator,

a trap in the form of a 60-ml. bottle should be attached between the generator and the bubbling tube.

*H<sub>2</sub>S is a poison.* Therefore, all H<sub>2</sub>S treatment should be carried out under a good hood. If H<sub>2</sub>S gas escapes into the room, the H<sub>2</sub>S treatment should be discontinued until ventilation is satisfactory.

3. If the solution being analyzed is a copper-arsenic group "known" or "unknown" containing only cations of the copper-arsenic group, this decantate can be discarded.

4. The precipitation of the copper-arsenic group is complicated by the fact that certain of the sulfides are precipitated only from solutions of high acid content, whereas others precipitate only when the acid concentration is relatively low. For example, arsenic precipitates best from a hot strongly acid solution, whereas cadmium, lead, and tin II precipitate from weakly acid solutions. When the acid concentration of the solution is changed gradually from very strongly acid to weakly acid, the order in which the sulfides of the copper-arsenic group precipitate is approximately as follows: As<sub>2</sub>S<sub>6</sub>, As<sub>2</sub>S<sub>3</sub>, HgS, CuS, Sb<sub>2</sub>S<sub>3</sub>, Bi<sub>2</sub>S<sub>3</sub>, SnS<sub>2</sub>, CdS, PbS, and SnS. Therefore the H<sub>2</sub>S precipitation is carried out first in a hot strongly acid solution, then in a moderately acid solution, and finally in a cold dilute solution whose acid concentration is about 1.5N.

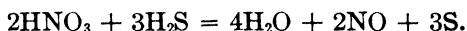
If the solution were neutral or very weakly acid, sulfides of the aluminum-nickel group, such as FeS, MnS, NiS, and CoS, also would be precipitated. Thus it is imperative that the acidity of the solution be carefully controlled during the precipitation of the group.

The group "known" and "unknown" solutions and the decantate from the silver group contain an unknown amount of acid. This acid is removed by evaporation to dryness in the first step in Procedure 5. Then a specific amount of hydrochloric acid and water is added. This method gives a solution of the proper acidity for the H<sub>2</sub>S precipitation.

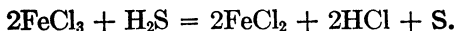
5. Six drops of 6N HCl are added before evaporation to dryness in order that any HNO<sub>3</sub> present may be destroyed in accordance with the following equation:



Nitric acid, if present, would oxidize the H<sub>2</sub>S, S being precipitated:



Other oxidizing agents, such as FeCl<sub>3</sub> or K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, may be present in a solution to be analyzed. They would react with H<sub>2</sub>S in acid solution as follows:

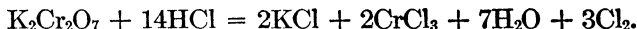


(The color changes from reddish yellow to the yellowish white of finely divided sulfur.)

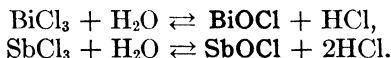


(The color changes from the orange red of  $\text{Cr}_2\text{O}_7^{--}$  to the green of  $\text{Cr}^{+++}$ .)

$\text{FeCl}_3$  would not be affected by evaporation with 6N HCl.  $\text{K}_2\text{Cr}_2\text{O}_7$  would be reduced as follows:



6. If a solution containing members of the copper-arsenic group is diluted with water, a milky-white suspension may result because of the formation, by hydrolysis, of the insoluble white basic salts of bismuth and antimony according to the following equations:



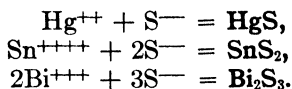
If the milky solution is treated with HCl, the milky solution will disappear because the equilibrium point in these two reactions has been shifted to the left.

7. It is to be noted that lead and mercury appear in the copper-arsenic group as well as in the silver group. Lead chloride is somewhat soluble in dilute HCl. For that reason, lead ions are not completely precipitated in the silver group and are carried over into the copper-arsenic group. Mercury occurs in the monovalent and bivalent state. Although  $\text{Hg}_2\text{Cl}_2$  is very insoluble in dilute HCl,  $\text{HgCl}_2$  is very soluble. Therefore mercury II is not precipitated in the silver group.

8. The sulfides of mercury, lead, bismuth, copper, and tin II are dark brown or black.  $\text{CdS}$ ,  $\text{SnS}_2$ ,  $\text{As}_2\text{S}_3$ , and  $\text{As}_2\text{S}_5$  are yellow.  $\text{Sb}_2\text{S}_3$  and  $\text{Sb}_2\text{S}_5$  are orange.

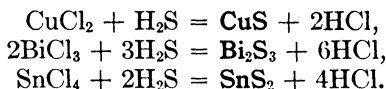
9.  $\text{CuCl}_2$  is green in concentrated solution and blue in dilute solution. The chlorides of all other members of the copper-arsenic group form colorless solutions except that  $\text{BiCl}_3$  and  $\text{SbCl}_3$  hydrolyze as explained in Note 6. The complete absence of any green or blue color in an unknown solution shows the absence of copper.

10. The sulfides of the metals are formed as a result of combination of the metallic ion (cation) with the sulfide ion:

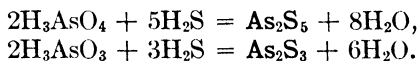




The molecular equations for these precipitation reactions may be represented as follows:



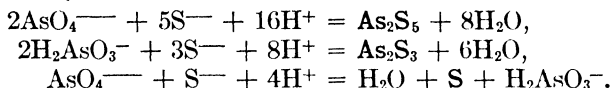
Arsenic is rarely if ever present in a solution as  $\text{As}^{+++}$ ,  $\text{As}^{++++}$ ,  $\text{AsCl}_3$ , or  $\text{AsCl}_5$ . Usually it is present as the arsenate ( $\text{AsO}_4^{---}$ ) or the arsenite ( $\text{H}_2\text{AsO}_3^-$ ). When it is present as arsenate or arsenite, the sulfides are precipitated according to the following equations:



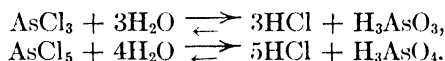
Some arsenate may be reduced by  $\text{H}_2\text{S}$  to arsenite:



The  $\text{H}_3\text{AsO}_3$  then reacts with  $\text{H}_2\text{S}$  to form  $\text{As}_2\text{S}_3$  as noted above. The above three equations may be represented, ionically, as follows:

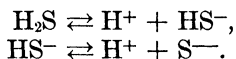


11. Arsenic is predominately nonmetallic in character. Hence its existence as the anions, arsenate ( $\text{AsO}_4^{---}$ ), and arsenite ( $\text{H}_2\text{AsO}_3^-$ ). Furthermore if arsenic chlorides are added to water, they behave like typical nonmetal chlorides in that they hydrolyze strongly to form  $\text{HCl}$  and the corresponding arsenic acid, as shown in the following equations:



12. Attention has been called, in Note 4, to the fact that arsenic sulfides precipitate only in strongly acid solutions and that the precipitation of  $\text{As}_2\text{S}_5$  requires higher acidity than does the precipitation of  $\text{As}_2\text{S}_3$ . An examination of the ionic equations for the reaction of arsenate and arsenite with sulfide ions (see end of Note 10) explains why a high concentration of  $\text{HCl}$  is required. The precipitation of  $\text{As}_2\text{S}_5$  from  $\text{AsO}_4^{---}$  requires 16 hydrogen ions for each mole of  $\text{As}_2\text{S}_5$  formed, whereas 8 hydrogen ions are required for each mole of  $\text{As}_2\text{S}_3$  formed from  $\text{H}_2\text{AsO}_3^-$ . Even though the arsenic may have originally existed as  $\text{AsCl}_3$  or  $\text{AsCl}_5$ , it is immediately changed to arsenite or arsenate when dissolved in water as shown in Note 11.

13. The sulfide ions required for the precipitation of the copper-arsenic group sulfides as shown in the equations in Note 10 are derived from the ionization of the weak acid,  $\text{H}_2\text{S}$ , which is formed when  $\text{H}_2\text{S}$  gas is dissolved in water solution. The ionization of  $\text{H}_2\text{S}$  takes place in these two stages:



For the purposes of this discussion, however, the two stages may be combined into one equation, as follows:



If the hydrogen ion concentration (acidity) of a saturated solution of  $\text{H}_2\text{S}$  is increased by addition of  $\text{HCl}$ , the equilibrium point in the above reaction is shifted to the left, with a resulting decrease in the  $\text{S}^{--}$  ion concentration. If the concentration of  $\text{H}^+$  is decreased by dilution of the saturated solution of  $\text{H}_2\text{S}$  with water, the equilibrium point is shifted to the right, with a resulting increase in the  $\text{S}^{--}$  concentration. That is, in a saturated solution of  $\text{H}_2\text{S}$ , the greater the  $\text{H}^+$  concentration, the smaller the  $\text{S}^{--}$  concentration; and the greater the  $\text{S}^{--}$  concentration, the smaller the  $\text{H}^+$  concentration.

To get complete precipitation of the cations of the copper-arsenic group as sulfides, the concentration of the sulfide ion, which is the group-reagent ion, should be as high as possible; to get a high  $\text{S}^{--}$  concentration, the  $\text{H}^+$  concentration should be as low as possible. There are two factors that modify the application of this rule. The conversion of arsenites and arsenates to sulfides requires a high concentration of hydrogen ion ( $\text{HCl}$ ) as explained in Note 12. At the other extreme, if the acidity is too low, the sulfide ion concentration will be so high that the sulfides of iron, zinc, manganese, cobalt, and nickel will also precipitate. By varying the concentration of the  $\text{HCl}$  solution from 12N to approximately 1.5N complete precipitation of all cations of the copper-arsenic group is obtained without precipitation of the cations of the following group.

The statement in Note 4 that  $\text{HgS}$  will precipitate from a strongly acid solution does not mean that it will not precipitate from a less acid solution; it will precipitate more readily and more completely from a solution of lesser acidity.

14. The statement has been made that, as a general rule, the water-insoluble salt of a weak acid will dissolve in a strong acid (see Note 8, Procedure 4). By this rule the metal sulfides should dissolve in  $\text{HCl}$ . The fact that they do not dissolve means that their normal solubility

in water is so very small that not even a strong acid can give a concentration of hydrogen ions sufficiently high to cause them to go into solution.

### SEPARATION OF THE COPPER GROUP FROM THE ARSENIC GROUP

The sulfides of arsenic, antimony, and tin are soluble in a solution of ammonium polysulfide. The sulfides of copper, lead, mercury, bismuth, and cadmium are insoluble. This fact is the basis for the separation of the copper group from the arsenic group.

#### Procedure 6: Separation of the copper group from the arsenic group

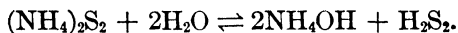
To the test tube containing the precipitate from Procedure 5 add 10 drops of ammonium polysulfide (see Note 1), mix thoroughly, and then heat the tube in a water bath (see Note 2) at 50–70°C. for 2 minutes, stirring the contents of the tube while heating. Wash down with a few drops of cold ammonium polysulfide any precipitate adhering to the sides of the tube, centrifuge, and decant, saving the decantate for Procedure 11. Repeat the treatment of the precipitate with a second 10-drop portion of ammonium polysulfide. Combine the second decantate with the first and save them in a stoppered test tube for Procedure 11. Wash the precipitate twice with 15-drop portions of hot water to which 5 drops of  $\text{N NH}_4\text{NO}_3$  or  $\text{NH}_4\text{Cl}$  are added; analyze this precipitate, which may consist of the sulfides of mercury II, lead, bismuth, copper, and cadmium, according to Procedure 7.

#### NOTES

1. It is absolutely essential that the ammonium polysulfide reagent be of good quality. Otherwise, proper separation of arsenic, antimony, and tin sulfides from the other sulfides will not be attained. Good-quality ammonium polysulfide should not have a residue of sulfur in the bottle; furthermore it should smell strongly of excess ammonia. If a residue of sulfur is present in the ammonium polysulfide bottle, have the reagent replaced by a fresh supply.

2. The water bath consists of a 100-ml. beaker fitted with a metal cover into which four holes have been stamped; each hole is large enough to hold a small test tube. The beaker is filled about three-fourths full of water and is placed on a wire screen supported on a ring stand. By proper adjustment of the Bunsen burner the temperature of the water can be held in the 50–70°C. range. If a thermometer is suspended from a clamp attached to the ring stand in such a way that the bulb of the thermometer is immersed in the hot water, the temperature of the bath can be observed very easily.

3. Ammonium polysulfide is prepared by dissolving sulfur in a solution of ammonium sulfide. It contains a mixture of the following compounds:  $(\text{NH}_4)_2\text{S}$ ,  $(\text{NH}_4)_2\text{S}_2$ ,  $(\text{NH}_4)_2\text{S}_3$ ,  $(\text{NH}_4)_2\text{S}_4$ ,  $(\text{NH}_4)_2\text{S}_5$ ; hence the name "polysulfide." Since  $(\text{NH}_4)_2\text{S}_2$  is present in appreciable quantity, this compound is arbitrarily chosen in writing equations for reactions in which ammonium polysulfide takes part. Ammonium polysulfide is always strongly alkaline because of the presence of excess  $\text{NH}_4\text{OH}$ .  $(\text{NH}_4)_2\text{S}_2$  hydrolyzes in water as follows:



The presence of excess  $\text{NH}_4\text{OH}$  greatly reduces the extent of this hydrolysis. Loss of  $\text{NH}_3$  by escape from an open reagent bottle promotes hydrolysis.

$(\text{NH}_4)_2\text{S}_2$  tends to decompose completely at higher temperatures because the  $\text{NH}_4\text{OH}$  and  $\text{H}_2\text{S}_2$  formed as a result of hydrolysis, being unstable, break down to form  $\text{NH}_3$  and  $\text{H}_2\text{S}$ , which are driven off as gases, and  $\text{S}$ , which precipitates:

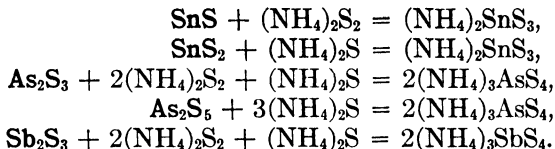


Ammonium polysulfide is oxidized on standing in the air, sulfur being deposited:

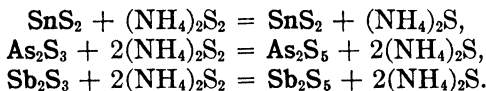


As a result of the combined effects of hydrolysis and oxidation,  $(\text{NH}_4)_2\text{S}_2$  deteriorates quite rapidly unless kept in well-stoppered bottles. Since deterioration is accompanied by precipitation of sulfur, its incidence is easily observed. As soon as sulfur begins to precipitate, the contents of the reagent bottle should be replaced by fresh solution.

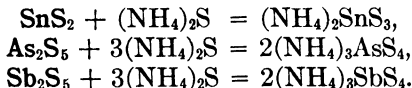
4. Ammonium polysulfide dissolves the sulfides of arsenic, antimony, and tin in accordance with the following equations:



The valence of tin in ammonium thiostannate,  $(\text{NH}_4)_2\text{SnS}_3$ , is +4, of arsenic in ammonium thioarsenate,  $(\text{NH}_4)_3\text{AsS}_4$ , is +5, and of antimony in ammonium thioantimonate,  $(\text{NH}_4)_3\text{SbS}_4$ , is +5.  $(\text{NH}_4)_2\text{S}_2$  has oxidized tin, arsenic, and antimony to their high valences. Notes 1 and 2 of Procedure 11 point out the fact that the sulfides  $\text{SnS}_2$ ,  $\text{As}_2\text{S}_5$ , and  $\text{Sb}_2\text{S}_5$  are the "acid anhydrides" of the thioacids  $\text{H}_2\text{SnS}_3$ ,  $\text{H}_3\text{AsS}_4$ , and  $\text{H}_3\text{SbS}_4$  just as  $\text{SnO}_2$ ,  $\text{As}_2\text{O}_5$ , and  $\text{Sb}_2\text{O}_5$  are the acid anhydrides of the acids  $\text{H}_2\text{SnO}_3$ ,  $\text{H}_3\text{AsO}_4$ , and  $\text{H}_3\text{SbO}_4$ .  $\text{H}_2\text{S}$  plays the same role in the formation of the thioacids that  $\text{H}_2\text{O}$  does in the formation of the oxygen acids.  $(\text{NH}_4)_2\text{S}$ ,  $\text{HgS}$ ,  $\text{CuS}$ ,  $\text{CdS}$ ,  $\text{PbS}$ , and  $\text{Bi}_2\text{S}_3$  are "basic anhydrides" in the sulfur (thio) system, just as  $(\text{NH}_4)_2\text{O}$ ,  $\text{CaO}$ , and  $\text{Na}_2\text{O}$  are basic anhydrides (basic oxides) in the oxygen system. Just as a basic anhydride,  $\text{Na}_2\text{O}$ , will react with an acid anhydride such as  $\text{SiO}_2$  to form the soluble salt  $\text{Na}_2\text{SiO}_3$ , so will the basic anhydride  $(\text{NH}_4)_2\text{S}$  react with the acid anhydrides  $\text{SnS}_2$ ,  $\text{As}_2\text{S}_5$ , and  $\text{Sb}_2\text{S}_5$  to form the soluble salts  $(\text{NH}_4)_2\text{SnS}_3$ ,  $(\text{NH}_4)_3\text{AsS}_4$ , and  $(\text{NH}_4)_3\text{SbS}_4$ . On the other hand, the basic anhydride  $(\text{NH}_4)_2\text{S}$  will not react with the basic anhydrides  $\text{HgS}$ ,  $\text{CuS}$ ,  $\text{CdS}$ ,  $\text{PbS}$ , and  $\text{Bi}_2\text{S}_3$ . We may state, therefore, that the separation of tin, arsenic, and antimony from mercury, lead, copper, cadmium, and bismuth depends on the fact that  $\text{SnS}_2$ ,  $\text{As}_2\text{S}_5$ , and  $\text{Sb}_2\text{S}_5$  are acid anhydrides, whereas  $\text{HgS}$ ,  $\text{PbS}$ ,  $\text{CuS}$ ,  $\text{CdS}$ , and  $\text{Bi}_2\text{S}_3$  are basic anhydrides. If the tin, arsenic, and antimony are present, initially, as  $\text{SnS}$ ,  $\text{As}_2\text{S}_3$ , and  $\text{Sb}_2\text{S}_3$ , they are first oxidized to  $\text{SnS}_2$ ,  $\text{As}_2\text{S}_5$ , and  $\text{Sb}_2\text{S}_5$ , as follows:



The  $\text{SnS}_2$ ,  $\text{As}_2\text{S}_5$ , and  $\text{Sb}_2\text{S}_5$  are then dissolved by  $(\text{NH}_4)_2\text{S}$  as follows:



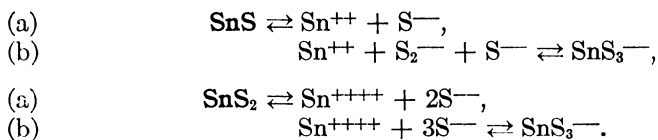
The five equations at the beginning of this note represent the over-all reactions.

5. At higher temperatures, ammonium polysulfide dissolves ap-

preciable quantities of copper sulfide and small quantities of mercuric sulfide. For this reason it is imperative that the temperature be held at or near 60°.

6. Antimony V does not ordinarily exist in solution, its oxidation state of 5 being very unstable. Antimony III is, however, converted to antimony V  $[(\text{NH}_4)_3\text{SbS}_4]$  by treatment with  $(\text{NH}_4)_2\text{S}_2$ .

7. The dissolving of  $\text{SnS}$ ,  $\text{SnS}_2$ ,  $\text{As}_2\text{S}_3$ ,  $\text{As}_2\text{S}_5$ , and  $\text{Sb}_2\text{S}_3$  by ammonium polysulfide may be interpreted by the following equations, in accordance with the rule given in Note 8, Procedure 4:



The  $\text{S}_2^{--}$  and  $\text{S}^{--}$  ions are derived from the ionization of  $(\text{NH}_4)_2\text{S}_2$  and  $(\text{NH}_4)_2\text{S}$ .

### SEPARATION OF MERCURY FROM LEAD, BISMUTH, COPPER, AND CADMIUM

The sulfides of copper, bismuth, cadmium, and lead are soluble in warm dilute  $\text{HNO}_3$ .  $\text{HgS}$  is insoluble. The separation of mercury from lead, bismuth, copper, and cadmium is based on this fact.

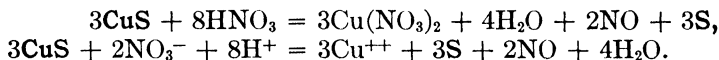
#### Procedure 7: Separation and detection of mercury II

Add 15 drops of 3N  $\text{HNO}_3$  to the test tube containing the precipitate from Procedure 6, mix thoroughly, and boil gently for about one minute or until all reaction ceases. Replenish the  $\text{HNO}_3$  if necessary. Wash down the sides of the tube with a few drops of water, centrifuge, and decant into a casserole, saving this decantate for Procedure 8. Wash the precipitate twice with 15-drop portions of water made acidic with a drop of 3N  $\text{HNO}_3$ . Treat this precipitate with 6 drops of 12N  $\text{HCl}$  and 2 drops of 16N  $\text{HNO}_3$ , mix thoroughly and heat slightly but do not boil. Add 10 drops of hot water and boil gently for about 30 seconds. Cool by holding the test tube under the water tap, then centrifuge. To the cool supernatant solution

in the test tube add 2–5 drops of  $\text{SnCl}_2$  solution. A white or gray precipitate ( $\text{Hg}_2\text{Cl}_2 + \text{Hg}$ ) proves the presence of mercury II.

### NOTES

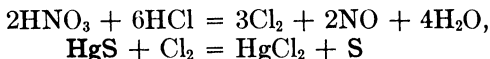
1. The sulfides of lead, copper, bismuth, and cadmium dissolve in  $\text{HNO}_3$  in accordance with the following equations:



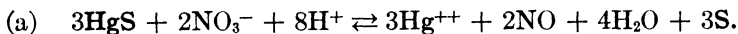
The relationship between a molecular equation and the corresponding ionic equation is illustrated by these two equations. Although the reactions in qualitative analysis are almost exclusively ionic in character, the complete picture of the reagents used as well as the reactions that take place is best shown by the use of molecular equations. Accordingly, molecular equations will be used hereafter in most instances except in those cases in which a presentation of the ionic equation is deemed necessary for elucidation of the reaction. The student is, however, expected to be able to present the ionic as well as the molecular equation.

2. If the  $\text{HNO}_3$  is too concentrated, it will dissolve some of the  $\text{HgS}$ . In addition, it may oxidize  $\text{PbS}$  to  $\text{PbSO}_4$ , which will remain as a residue mixed with the  $\text{HgS}$ .

3. The dissolving of  $\text{HgS}$  is best accomplished by treating it with reagents that will liberate chlorine. When  $\text{HNO}_3$  and  $\text{HCl}$  are used, the following reactions probably occur:



There is strong evidence to indicate that the role of  $\text{HCl}$  in the action of aqua regia on metals and metal sulfides involves the reaction of  $\text{Cl}^-$  ion with the cation to form a stable complex ion (see Note 8, Procedure 4). The nitric acid first reacts according to equation (a):

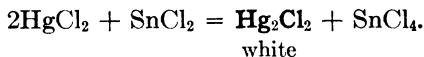


The  $\text{Cl}^-$  ions (from  $\text{HCl}$ ) then react with the cation as follows:

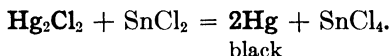


The equilibrium point in reaction (a) is thereby shifted to the right; this shift promotes the conversion of the metal (or metal sulfide) to the cation.

4. The extent to which  $\text{HgCl}_2$  is reduced by  $\text{SnCl}_2$  depends on the relative amounts of the two compounds present. If  $\text{HgCl}_2$  is present in large excess, it is reduced mostly to  $\text{Hg}_2\text{Cl}_2$  as follows:



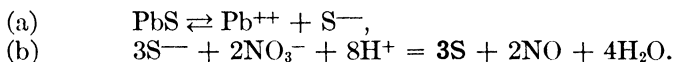
If an excess of  $\text{SnCl}_2$  is present, the  $\text{Hg}_2\text{Cl}_2$  which is first formed according to the above reaction is further reduced to  $\text{Hg}$  as follows:



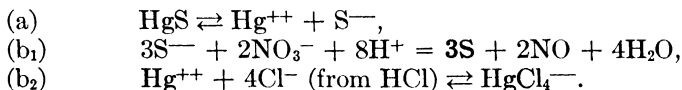
Since both reactions generally occur, the final precipitate is a gray mixture of  $\text{Hg}$  and  $\text{Hg}_2\text{Cl}_2$ .

These two equations illustrate the fact that tin II compounds are powerful reducing agents.

5. The dissolving of  $\text{CuS}$ ,  $\text{PbS}$ ,  $\text{CdS}$ , and  $\text{Bi}_2\text{S}_3$  by  $\text{HNO}_3$  may be interpreted in accordance with the rule given in Note 8, Procedure 4:



The dissolving of  $\text{HgS}$  by aqua regia (see Note 3) may be interpreted as involving the following equations:



### SEPARATION OF LEAD FROM BISMUTH, COPPER, AND CADMIUM

Lead sulfate is insoluble in water. The sulfates of bismuth, copper, and cadmium are soluble. This fact is the basis for the separation of lead ions from bismuth, copper, and cadmium ions.

#### Procedure 8: Separation and detection of lead

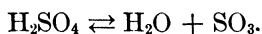
Add 4 drops of 36N  $\text{H}_2\text{SO}_4$  to the casserole containing the decantate from Procedure 7 and evaporate carefully to a volume of 3 or 4 drops. Cool, add 15 drops of cold water, swish, and stir the contents until all material in the casserole is dissolved or suspended; then transfer it quickly to a test tube



before the suspended material has a chance to settle; swish the casserole with 4 drops of cold water and transfer this washing to the same test tube. Cool under the water tap. A white precipitate (**PbSO<sub>4</sub>**) in the form of a fine suspension proves the presence of lead. Centrifuge until the supernatant liquid is clear and decant into a test tube, saving this decantate for Procedure 9. Wash the precipitate twice with 10-drop portions of cold water. To the washed precipitate in the test tube add 4 drops of 4N **NH<sub>4</sub>C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>** and stir for 10 seconds; then add 2 drops of N **K<sub>2</sub>CrO<sub>4</sub>**. A yellow precipitate (**PbCrO<sub>4</sub>**) confirms the presence of lead.

#### NOTES

1. **PbSO<sub>4</sub>** is appreciably soluble in concentrated **HNO<sub>3</sub>**. For this reason, **HNO<sub>3</sub>** must be removed before **PbSO<sub>4</sub>** will precipitate. When a solution containing **H<sub>2</sub>SO<sub>4</sub>**, **HNO<sub>3</sub>**, and water is boiled, the water and **HNO<sub>3</sub>** are first driven off because they boil at comparatively low temperatures (100°–120°). After they are removed, further heating results in boiling the **H<sub>2</sub>SO<sub>4</sub>** that remains (boiling point of sulfuric acid is 338°). At its boiling temperature the **H<sub>2</sub>SO<sub>4</sub>** decomposes to a slight extent:



**SO<sub>3</sub>** fumes strongly in moist air. Therefore, dense white fumes may form at the end of the evaporation.

2. When the solution which has been boiled down with concentrated **H<sub>2</sub>SO<sub>4</sub>** is cooled, sulfates of bismuth, copper, and cadmium may crystallize out. However, they are soluble in dilute **H<sub>2</sub>SO<sub>4</sub>** and will dissolve when the water is added. **PbSO<sub>4</sub>**, on the other hand, is rather soluble in concentrated **H<sub>2</sub>SO<sub>4</sub>**, forming the acid sulfate, **Pb(HSO<sub>4</sub>)<sub>2</sub>**. On dilution with water, the soluble acid sulfate is decomposed to form insoluble **PbSO<sub>4</sub>**.

3. The precipitate of **PbSO<sub>4</sub>** is very finely divided. The sulfates of bismuth, copper, and cadmium form relatively large crystals.

4. Since lead is largely removed in the silver group, only very small quantities will ordinarily appear in the copper-arsenic group. For this reason, the test for lead is not as pronounced as the tests for other cations in this group.

5. **PbSO<sub>4</sub>** dissolves in ammonium acetate because the **Pb(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub>** formed in the reaction, **PbSO<sub>4</sub> + 2NH<sub>4</sub>C<sub>2</sub>H<sub>3</sub>O<sub>2</sub> = Pb(C<sub>2</sub>H<sub>3</sub>O<sub>2</sub>)<sub>2</sub> +**

$(\text{NH}_4)_2\text{SO}_4$ , is only slightly ionized, giving, therefore, a solution with a very low concentration of lead ions.  $\text{PbCrO}_4$  is less soluble than  $\text{PbSO}_4$ . Therefore, when  $\text{K}_2\text{CrO}_4$  is added to the solution formed by adding  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  to  $\text{PbSO}_4$ , a precipitate of  $\text{PbCrO}_4$  is formed even though the concentration of lead ions in the solution is very low.

### SEPARATION OF BISMUTH FROM COPPER AND CADMIUM

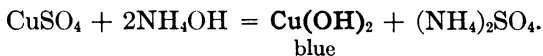
The addition of  $\text{NH}_4\text{OH}$  to a solution containing bismuth, copper, and cadmium ions first precipitates the hydroxides of all three metals. The hydroxides of copper and cadmium, however, dissolve in an excess of  $\text{NH}_4\text{OH}$ , whereas the hydroxide of bismuth does not; the separation of bismuth ions from copper and cadmium ions is based on this fact.

#### Procedure 9: Separation and detection of bismuth

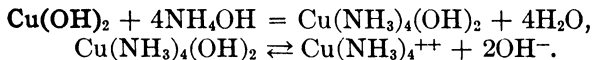
To the decantate from Procedure 8 add 15N  $\text{NH}_4\text{OH}$ , dropwise, with constant mixing, until it becomes distinctly alkaline. Stir for one minute. Centrifuge and decant, saving the decantate for Procedure 10. Wash the precipitate twice with 15-drop portions of hot water. To the washed precipitate add 3 drops of 8N  $\text{NaOH}$  and 2 drops of 0.5N  $\text{SnCl}_2$  and stir. A jet-black precipitate (Bi) proves the presence of bismuth.

#### NOTES

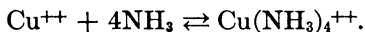
1. When  $\text{NH}_4\text{OH}$  is added to a solution containing copper ions,  $\text{Cu}(\text{OH})_2$  is first precipitated:



An excess of  $\text{NH}_4\text{OH}$ , however, dissolves the  $\text{Cu}(\text{OH})_2$  to give a deep-blue solution in which Cu is present as the complex ion,  $\text{Cu}(\text{NH}_3)_4^{++}$ :

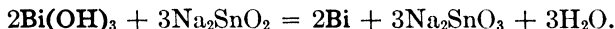


The simple ionic equation for the over-all reaction is



Cadmium behaves in the same manner,  $\text{Cd}(\text{NH}_3)_4^{++}$  being formed.  $\text{Cd}(\text{OH})_2$  dissolves quite slowly in excess  $\text{NH}_4\text{OH}$ ; therefore, the solution is stirred for one minute to ensure complete solution of  $\text{Cd}(\text{OH})_2$ . Similar complexes will be met with in the case of the ions of nickel, cobalt, and zinc.  $\text{Ag}(\text{NH}_3)_2^+$  was formed in the analysis of the silver group (see Note 8, Procedure 4).

2. The formation of the black precipitate of bismuth results from the action of  $\text{Na}_2\text{SnO}_2$  (sodium stannite) on  $\text{Bi}(\text{OH})_3$  as follows:

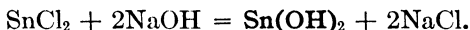


The  $\text{Na}_2\text{SnO}_2$  was formed when the  $\text{SnCl}_2$ , added as the final reagent, reacted with the excess of  $\text{NaOH}$  which had been added previously:

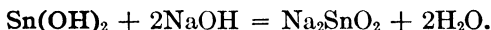


The reaction of  $\text{Na}_2\text{SnO}_2$  with  $\text{Bi}(\text{OH})_3$  serves further to illustrate the reducing character of tin II compounds.

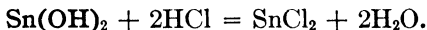
3. The formation of  $\text{Na}_2\text{SnO}_2$  by the action of  $\text{NaOH}$  on  $\text{SnCl}_2$  is a two-stage reaction. If  $\text{NaOH}$  is added, dropwise, to a solution of  $\text{SnCl}_2$ , a white precipitate of  $\text{Sn}(\text{OH})_2$  is first formed:



This white precipitate redissolves in more  $\text{NaOH}$  to form a clear colorless solution of the soluble salt,  $\text{Na}_2\text{SnO}_2$ :



4.  $\text{Sn}(\text{OH})_2$  dissolves in  $\text{HCl}$  to form the salt  $\text{SnCl}_2$ :

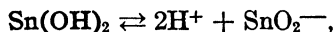


In this reaction it acts as a base.

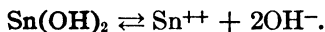
$\text{Sn}(\text{OH})_2$ , in its reaction with the base,  $\text{NaOH}$ , to form the salt,  $\text{Na}_2\text{SnO}_2$  (see Note 3 above), reacts as an acid ( $\text{H}_2\text{SnO}_2$ ).

Hydroxides, such as  $\text{Sn}(\text{OH})_2$ , which act as acids in the presence of strong bases and as bases in the presence of strong acids, are called *amphoteric hydroxides*. In addition to  $\text{Sn}(\text{OH})_2$ , the following hydroxides are amphoteric:  $\text{Al}(\text{OH})_3$ ,  $\text{Cr}(\text{OH})_3$ ,  $\text{Zn}(\text{OH})_2$ ,  $\text{Pb}(\text{OH})_2$ , and  $\text{Sb}(\text{OH})_3$ .

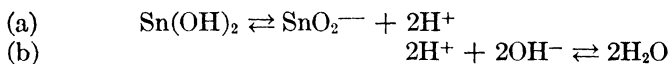
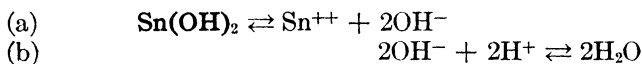
5. The amphoteric behavior of  $\text{Sn}(\text{OH})_2$  indicates that it ionizes as an acid:



and also as a base:

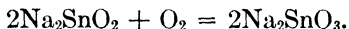


The dissolving of  $\text{Sn}(\text{OH})_2$  by either a strong acid or a strong base is then readily interpreted (see Note 8, Procedure 4).

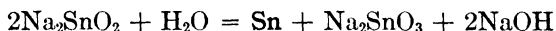


6. Sodium stannite will reduce the hydroxides of antimony, lead, copper, and cadmium to the corresponding metal. These hydroxides, however, are reduced slowly and the metallic deposit is not jet-black, whereas  $\text{Bi}(\text{OH})_3$  is reduced instantly and forms a jet-black deposit of metallic bismuth.

7. On standing in contact with air,  $\text{Na}_2\text{SnO}_2$  is rapidly oxidized to  $\text{Na}_2\text{SnO}_3$  (sodium stannate) as follows:



Furthermore,  $\text{Na}_2\text{SnO}_2$  decomposes in solution as follows:



For these reasons  $\text{Na}_2\text{SnO}_2$  is not kept on the shelf as a reagent but is formed by the action of  $\text{NaOH}$  on  $\text{SnCl}_2$  at the time it is to be used.

8. A reaction of the type illustrated in the second equation of Note 7, in which a compound acts as both an oxidizing agent and a reducing agent, is referred to as *disproportionation*. The  $\text{SnO}_2^-$  in one molecule of  $\text{Na}_2\text{SnO}_2$  is reduced to  $\text{Sn}$ , whereas the  $\text{SnO}_2^-$  in the second molecule is oxidized to  $\text{SnO}_3^-$ .

9. The stannate ion is believed to exist in solution as  $\text{Sn}(\text{OH})_6^-$  rather than  $\text{SnO}_3^-$ .  $\text{Sn}(\text{OH})_6^-$  may be looked upon as hydrated  $\text{SnO}_3^-$ .

## DETECTION OF COPPER AND CADMIUM

### Procedure 10: Separation and detection of copper and cadmium

(a) *Detection of copper.* If the decantate from Procedure 9 is colorless, copper is absent and need not be tested for; if the decantate is deep blue, because of the  $\text{Cu}(\text{NH}_3)_4^{++}$  ion, copper is present. Place 5 drops of this blue decantate in a clean test tube, add 5N  $\text{HC}_2\text{H}_3\text{O}_2$  until the deep-blue color just disappears, and then add 2 drops of N  $\text{K}_4\text{Fe}(\text{CN})_6$ . A red precipitate ( $\text{Cu}_2\text{Fe}(\text{CN})_6$ ) further confirms the presence of copper.

(b) *Detection of cadmium.* If copper is absent, treat the colorless decantate from Procedure 9 with  $\text{H}_2\text{S}$  for a few seconds. A yellow precipitate (**CdS**) proves the presence of cadmium. If copper is present, add N KCN, dropwise, to a 10-drop portion of the blue decantate until the blue color disappears. Treat with  $\text{H}_2\text{S}$  for a few seconds. A yellow precipitate (**CdS**) proves the presence of cadmium.

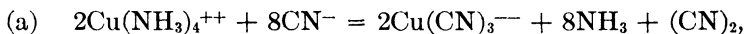
### NOTES

1. The blue color of  $\text{Cu}(\text{NH}_3)_4^{++}$  is visible when as little as 1 part of copper in 25,000 parts of water is present. The red precipitate of  $\text{Cu}_2\text{Fe}(\text{CN})_6$  will detect 1 part of copper in 1 million parts of water.

2.  $\text{Cu}_2\text{Fe}(\text{CN})_6$  is soluble in strong acids, such as  $\text{HCl}$  and  $\text{H}_2\text{SO}_4$ , but precipitates readily in the presence of a weak acid, such as acetic acid.  $\text{Cd}_2\text{Fe}(\text{CN})_6$  precipitates under the same conditions as does  $\text{Cu}_2\text{Fe}(\text{CN})_6$ , but the precipitate is white.

3. When excess KCN is added to a solution containing  $\text{Cu}(\text{NH}_3)_4^{++}$  and  $\text{Cd}(\text{NH}_3)_4^{++}$ , the complex ions  $\text{Cu}(\text{CN})_3^-$  and  $\text{Cd}(\text{CN})_4^-$  are formed. The  $\text{Cu}(\text{CN})_3^-$  ion is very stable and is only very slightly dissociated into  $\text{Cu}^+$  and  $3\text{CN}^-$  ions; the resulting concentration of  $\text{Cu}^+$  is so low that no precipitate of  $\text{Cu}_2\text{S}$  forms when  $\text{H}_2\text{S}$  is added. The  $\text{Cd}(\text{CN})_4^-$  ion is less stable and is appreciably dissociated into  $\text{Cd}^{++}$  and  $4\text{CN}^-$  ions; the resulting concentration of  $\text{Cd}^{++}$  is high enough for a precipitate of  $\text{CdS}$  to form when  $\text{H}_2\text{S}$  is added.

The reactions that take place when excess KCN ( $\text{K}^+ + \text{CN}^-$ ) is added are best represented by the following ionic equations:



It will be noted, in Equation (a), that the oxidation state (valence) of copper is reduced from +2 in  $\text{Cu}(\text{NH}_3)_4^{++}$  to +1 in  $\text{Cu}(\text{CN})_3^-$ . Cyanogen gas,  $(\text{CN})_2$ , is formed as a reduction product.

### Procedure 11: Reprecipitation of the sulfides of arsenic, antimony, and tin

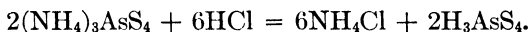
To the test tube containing the decantate from Procedure 6 add 1.5N  $\text{HCl}$ , with constant stirring, until the solution is just slightly acidic. (As long as each drop of 1.5N  $\text{HCl}$  keeps

on bringing down more precipitate, the solution is still alkaline; when no more precipitate forms, the solution is probably acidic.) (See note 1.) A large excess of HCl must be avoided. Centrifuge and decant, discarding the decantate. Wash the precipitate three times with hot water; analyze this precipitate according to Procedure 12.

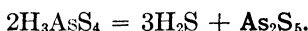
### NOTES

1. When 1.5N HCl is being added to reprecipitate the sulfides of arsenic, antimony, and tin, the volume of solution may sometimes exceed the capacity of the small test tube before the solution is acidic. In such an event simply pour off or draw off, and discard a bit of the solution.

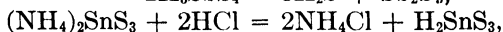
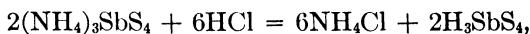
2. The addition of dilute HCl to the soluble thiosalts of the arsenic group reprecipitates the sulfides of the three elements in accordance with the following equation:



The compound  $\text{H}_3\text{AsS}_4$  is unstable and decomposes:



$(\text{NH}_4)_2\text{SnS}_3$  and  $(\text{NH}_4)_3\text{SbS}_4$  react in a similar manner:



3. The thiosalts are salts of thioacids. Their relation to the oxy-salts and the oxy-acids is shown below.

SULFUR SYSTEM			OXYGEN SYSTEM		
<i>Thiosalt</i>	<i>Thioacid</i>	<i>Acid</i> <i>"Anhydride"</i>	<i>Oxysalt</i>	<i>Oxyacid</i>	<i>Acid</i> <i>"Anhydride"</i>
$(\text{NH}_4)_2\text{SnS}_3$	$\text{H}_2\text{SnS}_3$	$\text{SnS}_2$	$(\text{NH}_4)_2\text{SnO}_3$	$\text{H}_2\text{SnO}_3$	$\text{SnO}_2$
$(\text{NH}_4)_3\text{AsS}_4$	$\text{H}_3\text{AsS}_4$	$\text{As}_2\text{S}_5$	$(\text{NH}_4)_3\text{AsO}_4$	$\text{H}_3\text{AsO}_4$	$\text{As}_2\text{O}_5$
$(\text{NH}_4)_3\text{SbS}_4$	$\text{H}_3\text{SbS}_4$	$\text{Sb}_2\text{S}_5$	$(\text{NH}_4)_3\text{SbO}_4$	$\text{H}_3\text{SbO}_4 \cdot 2\text{H}_2\text{O}$	$\text{Sb}_2\text{O}_5$

$(\text{H}_3\text{SbO}_4 \cdot 2\text{H}_2\text{O})$  may be represented as  $\text{H}_7\text{SbO}_6$ .)

4. It should be noted that whereas in the initial precipitation of the copper-arsenic group, arsenic, antimony, and tin may be present

as the high- and low-valenced sulfides ( $\text{As}_2\text{S}_3$ ,  $\text{As}_2\text{S}_5$ ,  $\text{Sb}_2\text{S}_3$ ,  $\text{SnS}$ ,  $\text{SnS}_2$ ), in the reprecipitation in Procedure 11 they appear only as the high-valenced compounds.  $(\text{NH}_4)_2\text{S}_2$  has oxidized the elements to their high valences.

5. The formation of a white precipitate on addition of dilute  $\text{HCl}$  in Procedure 11 is due to the liberation of sulfur from  $(\text{NH}_4)_2\text{S}_2$ :



If there is doubt whether this precipitate is sulfur or the arsenic group sulfides, a blank test should be run on some  $(\text{NH}_4)_2\text{S}_2$ .

6. In reprecipitating the arsenic group, a large excess of dilute  $\text{HCl}$  must be avoided, since  $\text{SnS}_2$  is appreciably soluble in high concentrations of this acid. Also, the precipitate of  $\text{SnS}_2$ ,  $\text{As}_2\text{S}_5$ , and  $\text{Sb}_2\text{S}_5$  should be decanted at once, since the  $\text{SnS}_2$  and  $\text{Sb}_2\text{S}_5$  will dissolve on standing.

7. A dark-colored decantate from Procedure 6 means that some  $\text{CuS}$ , and perhaps  $\text{HgS}$ , has been peptized by the  $(\text{NH}_4)_2\text{S}_2$ . If this decantate is allowed to stand for about 24 hours, the  $\text{CuS}$  and  $\text{HgS}$  will ordinarily settle out. The yellow supernatant liquid can then be decanted, leaving the  $\text{CuS}$  and  $\text{HgS}$  behind. If the decantate is to be analyzed immediately, add 5 drops of  $\text{N NH}_4\text{NO}_3$  or  $\text{NH}_4\text{Cl}$  to coagulate the  $\text{CuS}$  and  $\text{HgS}$ , mix thoroughly, centrifuge, and decant, discarding the precipitate.

## SEPARATION OF ARSENIC FROM ANTIMONY AND TIN

The separation of arsenic from antimony and tin depends on the fact that arsenic sulfide is insoluble in very concentrated  $\text{HCl}$ , whereas the sulfides of tin and antimony dissolve in the  $\text{HCl}$  to form soluble chlorides.

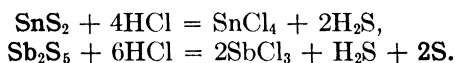
### Procedure 12: Separation of arsenic from antimony and tin

To the precipitate from Procedure 11, add 15 drops of 12N  $\text{HCl}$ , mix thoroughly, and heat the test tube in boiling water for two minutes, stirring frequently. Centrifuge; then decant very carefully, or withdraw, with a medicine dropper, as much as possible of the supernatant liquid. Save this liquid, which may contain antimony and tin, for Procedure 14. Wash the precipitate twice with 10-drop portions of 6N  $\text{HCl}$ , then

with three 15-drop portions of hot water. Be certain, when washing, that the mixture of precipitate and liquid is stirred thoroughly. Analyze the precipitate according to Procedure 13.

#### NOTES

1. Concentrated HCl dissolves  $\text{SnS}_2$  and  $\text{Sb}_2\text{S}_5$  as follows:



If considerable  $\text{Sb}_2\text{S}_5$  is present, a large amount of sulfur residue will remain after treatment with concentrated HCl.

Note that  $\text{Sb}^{++++}$  is reduced to  $\text{Sb}^{+++}$ .

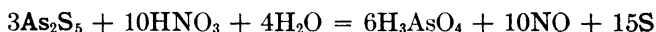
2. The precipitate ( $\text{As}_2\text{S}_5$ ) is first washed with 6N HCl, rather than with water, to remove all traces of  $\text{SbCl}_3$ .  $\text{SbCl}_3$  would react with water to form insoluble  $\text{SbOCl}$ , which would remain with the  $\text{As}_2\text{S}_5$ . The final washing with hot water is to remove all traces of HCl. Chloride, if present, would interfere with the confirmatory test for arsenic (Procedure 13) by forming a white precipitate of  $\text{AgCl}$ .

#### Procedure 13: Detection of arsenic

Add 10 drops of 16N  $\text{HNO}_3$  to the test tube containing the precipitate from Procedure 12 and boil gently for about one minute. Add 4–5 drops of water, centrifuge, and decant into a casserole, discarding any precipitate which remains in the test tube. Evaporate the solution in the casserole very carefully, just to dryness, being very careful not to bake. Allow to cool. Add 4 drops of 1N  $\text{NaC}_2\text{H}_3\text{O}_2$  and swish around in the casserole for about 10 seconds. Then add 2 drops of 0.25N  $\text{AgNO}_3$ . A reddish-brown precipitate ( $\text{Ag}_3\text{AsO}_4$ ) proves the presence of arsenic.

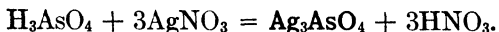
#### NOTES

1. The  $\text{As}_2\text{S}_5$  is dissolved by  $\text{HNO}_3$  as follows:



2.  $\text{Ag}_3\text{AsO}_4$  is formed in the confirmatory test for arsenic according to the following equation:





3.  $\text{Ag}_3\text{AsO}_4$  is soluble in the strong acid  $\text{HNO}_3$ ; it is, however, insoluble in a weakly acidic or neutral solution. Evaporation to dryness should remove all the  $\text{HNO}_3$ . As a precaution against the possibility of some  $\text{HNO}_3$  being left behind, the residue of  $\text{H}_3\text{AsO}_4$  is dissolved in  $\text{NaC}_2\text{H}_3\text{O}_2$  rather than in water.  $\text{NaC}_2\text{H}_3\text{O}_2$ , being the salt of a weak acid, will serve as a "buffer" for any  $\text{HNO}_3$  that might have remained; in the presence of  $\text{NaC}_2\text{H}_3\text{O}_2$ ,  $\text{Ag}_3\text{AsO}_4$  will precipitate even though a trace of  $\text{HNO}_3$  is present.  $\text{NaC}_2\text{H}_3\text{O}_2$  serves as a "buffer" as follows: The  $\text{C}_2\text{H}_3\text{O}_2^-$  ions from the strong electrolyte,  $\text{NaC}_2\text{H}_3\text{O}_2$ , combine with the  $\text{H}^+$  ions from  $\text{HNO}_3$  to form the weak acid,  $\text{HC}_2\text{H}_3\text{O}_2$ . This reaction reduces the  $\text{H}^+$  ion concentration to such a low value (makes the solution so weakly acidic) that  $\text{Ag}_3\text{AsO}_4$  will precipitate. Potassium acetate or ammonium acetate may be substituted for the sodium acetate.

4. The formation of a white precipitate ( $\text{AgCl}$ ) means that the  $\text{As}_2\text{S}_5$  was not washed free of chloride in Procedure 12.

#### Procedure 14: Detection of antimony and tin

(a) **Detection of antimony.** Transfer the decantate from Procedure 12 to a casserole, boil gently to remove any dissolved  $\text{H}_2\text{S}$ , then add 4–5 drops of cold water and mix thoroughly. Place a drop of this solution on a clean silver coin. Place a piece of mossy tin in this drop of solution. The rapid formation of a black deposit (**Sb**) on the silver coin proves the presence of antimony.

(b) **Detection of tin.** To the remainder of the solution in the casserole add a 1-in. piece of 28-gauge aluminum wire. Warm gently until the wire has dissolved; then boil gently for about two minutes or until the black precipitate either has all dissolved or appears not to be dissolving any more, replenishing the solution with 6N  $\text{HCl}$  if necessary. (If no black residue remains, the absence of antimony is proved; if a black residue (**Sb**) remains after 2 minutes' boiling, the presence of antimony is proved.) Transfer immediately to a test tube, cool under the water tap and centrifuge. Immediately add 2–3 drops of  $\text{HgCl}_2$  solution to the supernatant liquid; a white precipitate or suspension (**Hg<sub>2</sub>Cl<sub>2</sub>**) proves the presence of tin.

## NOTES

1. The solution that is used in making the confirmatory test for antimony must be free from  $\text{H}_2\text{S}$ ; otherwise a black stain of  $\text{Ag}_2\text{S}$  will be formed on the silver coin. Boiling the solution removes all  $\text{H}_2\text{S}$ .

2. The confirmatory test for antimony depends on the fact that when silver and tin are immersed in a solution of an electrolyte,  $\text{SbCl}_3$  in this case, a miniature battery is set up. The more active metal, tin, goes into solution giving  $\text{Sn}^{++}$  ions, while  $\text{Sb}^{+++}$  ions are driven out of solution and are deposited as metallic antimony on the less active metal, silver. The following reactions take place:

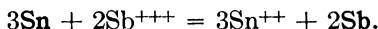


(These electrons are conducted away by the tin and cause it to become the negative plate in the battery.)

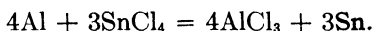


(Deposited on silver.)

The over-all reaction may be summarized as follows:

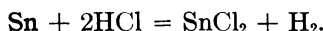


3. The aluminum is added to reduce  $\text{Sn}^{++++}$  to  $\text{Sn}^{++}$ . The reaction takes place as follows:



Excess aluminum is dissolved by the  $\text{HCl}$ .

The tin then dissolves in  $\text{HCl}$  to form  $\text{SnCl}_2$ :



The tin does not dissolve until all the aluminum has dissolved. Furthermore, since tin is not very active, being just above hydrogen in the activity series, it dissolves very slowly. For that reason the mixture must be boiled.

Since the tin II formed by the reaction of tin with  $\text{HCl}$  may eventually be oxidized by the oxygen of the air to tin IV, the test should be completed as rapidly as possible.

4. The chemistry of the final test for tin, in which  $\text{SnCl}_2$  reduces  $\text{HgCl}_2$  to  $\text{Hg} + \text{Hg}_2\text{Cl}_2$ , is the same as that involved in the confirmatory test for mercury (see Note 4, Procedure 7).

5. The metallic aluminum, added to the solution containing  $\text{SnCl}_4$  and  $\text{SbCl}_3$ , replaces antimony (black) as well as tin (gray). Antimony, being less active than hydrogen, does not dissolve in  $\text{HCl}$ .

6. A flame test for tin may be carried out as follows: Fill with cold water a test tube which is clean on the outside as well as on the inside. Dip the bottom of the test tube into the solution to be tested; then hold the bottom of the test tube in a hot, nonluminous Bunsen flame. A blue coloration in the flame, which appears to cling to the wall of the test tube, proves the presence of tin. A trial flame test for tin should first be run on a sample of tin salt solution from the reagent shelf so that the characteristic blue coloration may be recognized.

### Questions

1. Using the scheme of analysis as a guide, write equations for all reactions that take place in the copper-arsenic group.

2. Upon what fact or facts is each of the following based?

a. The separation of the cations of the copper-arsenic group from the cations of the groups that follow.

b. The separation of the copper group from the arsenic group.

c. The separation of mercury from lead, bismuth, copper, and cadmium.

d. The separation of lead from bismuth, copper, and cadmium.

e. The separation of bismuth from copper and cadmium.

f. The identification of cadmium in the presence of copper.

g. The confirmatory test for mercury.

h. The confirmatory test for bismuth.

i. The separation of arsenic from antimony and tin.

j. The confirmatory test for antimony.

k. The confirmatory test for tin.

3. What difficulties, if any, would arise under the following conditions in the precipitation of the copper-arsenic group?

a. If concentrated  $\text{HNO}_3$  were used in place of concentrated  $\text{HCl}$ .

b. If concentrated  $\text{H}_2\text{SO}_4$  were used in place of concentrated  $\text{HCl}$ .

c. If the  $\text{H}_2\text{S}$  treatment were made on a neutral solution rather than on the acid solution.

d. If the precipitation were carried out only in the presence of hot concentrated  $\text{HCl}$ , the successive dilutions with water being omitted.

e. If the precipitation were carried out only from a cold, weakly acid solution.

4. What difficulties, if any, would arise if, in the separation of the copper group from the arsenic group, the  $(\text{NH}_4)_2\text{S}_2$  were heated to  $100^\circ$  instead of to  $60^\circ$ ?

5. In the analysis of the copper group, what difficulties, if any, would arise under the following conditions?

a. If very concentrated  $\text{HNO}_3$  were used in the separation of mercury from lead, bismuth, copper, and cadmium.

b. If in the separation of bismuth from copper and cadmium, an excess of  $\text{NH}_4\text{OH}$  were not used.

c. If the solution were not stirred for one minute after the addition of excess  $\text{NH}_4\text{OH}$  in the separation of copper and cadmium from bismuth.

6. In the analysis of the arsenic group, what difficulties, if any, would arise if:

a. The filtrate containing the ammonium thiosalts were made strongly acid with  $\text{HCl}$ ?

b. The solution used in making the confirmatory test for antimony contained dissolved  $\text{H}_2\text{S}$ ?

7. Give the reason for each of the following:

a. Evaporation of the solution to dryness with 6N  $\text{HCl}$  as the first step in the copper-arsenic group analysis.

b. Avoiding baking the precipitate in the first evaporation step.

c. The presence of 12N  $\text{HCl}$  in the first stage of the  $\text{H}_2\text{S}$  precipitation.

d. Extensive dilution with water in the final stage of the  $\text{H}_2\text{S}$  precipitation.

e. Boiling the solution just before adding the  $\text{SnCl}_2$  in the confirmatory test for mercury.

f. Evaporation to a small volume followed by dilution with water in the separation of lead from bismuth, copper, and cadmium.

g. The addition of  $\text{KCN}$  before making the confirmatory test for cadmium.

h. The use of aluminum wire in the course of the confirmatory test for tin.

i. Boiling the solution for 2 minutes after the addition of the aluminum wire in the confirmatory test for tin.

j. The addition of  $\text{NaC}_2\text{H}_3\text{O}_2$  in the confirmatory test for arsenic.

k. Not keeping sodium stannite on the reagent shelf.

8. Point out, in detail, what takes place in each of the following. Give the equations for the significant reactions.

a. The confirmatory test for tin.

b. The confirmatory test for antimony.

c. The confirmatory test for bismuth.

d. The confirmatory test for cadmium in the presence of copper.

e. The confirmatory test for lead.

9. The precipitate formed in the confirmatory test for mercury II is sometimes white, sometimes gray, and sometimes black. Explain.

10. The concentration of sulfide ions in a saturated solution of  $\text{H}_2\text{S}$  varies with the hydrogen ion concentration of the solution. Explain.

11. Give the molecular or ionic equations to account for each of the following:

a. When  $\text{NaOH}$  is added, dropwise, to a solution of  $\text{SnCl}_2$ , a white precipitate is first formed, which disappears on further addition of  $\text{NaOH}$  to form a water-clear solution.

b. When  $\text{NH}_4\text{OH}$  is added, dropwise, to a solution of  $\text{CdCl}_2$ , a white precipitate is first formed, which disappears on further addition of  $\text{NH}_4\text{OH}$  to form a water-clear solution; when  $\text{HCl}$  is added, dropwise, to the water-clear solution, there is first formed a white precipitate, which disappears on further addition of  $\text{HCl}$  to give a clear solution.

12. When a green solution of  $\text{CuCl}_2$  is diluted with water, the color changes to a pale blue; addition of excess  $\text{NH}_4\text{OH}$  to the pale-blue solution makes it a deep blue; addition of  $\text{KCN}$  to this deep-blue solution causes it to become colorless. Account for the color changes.

13. Explain each of the following statements:

- (a)  $\text{Sn}(\text{OH})_2$  is amphoteric.
- (b)  $\text{SnS}_2$  is an acid anhydride.
- (c)  $\text{HgS}$  is a basic anhydride.

14. Point out where the following take place in the copper-arsenic group analysis and give the equations for the reactions:

a. Four reactions in which tin is oxidized from an oxidation state of 2 to an oxidation state of 4.

- b. One reaction in which mercury is reduced from 2 to 1.
- c. One reaction in which mercury is reduced from 1 to 0.
- d. One reaction in which bismuth is reduced from 3 to 0.
- e. One reaction in which tin is reduced from 4 to 0.
- f. One reaction in which antimony is reduced from 5 to 3.
- g. One reaction in which sulfur is oxidized from  $-2$  to 0.

15. Give the formula for a chemical substance which will:

- a. Form a precipitate with  $\text{SnCl}_2$  solution but not with  $\text{SnCl}_4$ .
- b. Form a precipitate with  $\text{Pb}(\text{NO}_3)_2$  solution but not with  $\text{Cu}(\text{NO}_3)_2$ .
- c. Form a precipitate with  $\text{H}_2\text{S}$  solution but not with  $\text{HCl}$ .
- d. Form a precipitate with  $(\text{NH}_4)_3\text{AsS}_4$  solution but not with  $\text{CuCl}_2$ .
- e. Form a precipitate with  $\text{SnCl}_2$  solution but not with  $\text{HgCl}_2$ .
- f. Form a precipitate with  $\text{Bi}_2(\text{SO}_4)_3$  solution but not with  $\text{CuSO}_4$ .
- g. Form a precipitate with  $\text{HNO}_3$  solution but not with  $\text{HCl}$ .
- h. Form a precipitate with  $\text{H}_2\text{SO}_4$  solution but not with  $\text{HNO}_3$ .
- i. Form a precipitate with  $\text{Pb}(\text{NO}_3)_2$  solution but not with  $\text{NaCl}$ .
- j. Form a precipitate with  $\text{CuCl}_2$  solution but not with  $\text{KCl}$ .
- k. Dissolve  $\text{As}_2\text{S}_3$  but not  $\text{HgS}$ .
- l. Dissolve  $\text{CuS}$  but not  $\text{HgS}$ .
- m. Dissolve  $\text{Sb}_2\text{S}_5$  but not  $\text{As}_2\text{S}_5$ .
- n. Dissolve  $\text{SnS}$  but not  $\text{PbS}$ .
- o. Dissolve  $\text{Pb}(\text{NO}_3)_2$  but not  $\text{PbS}$ .
- p. Dissolve  $\text{HgCl}_2$  but not  $\text{Hg}_2\text{Cl}_2$ .
- q. Oxidize  $\text{SnO}_2^-$  to  $\text{SnO}_3^-$ .
- r. Reduce  $\text{Hg}^{++}$  to  $\text{Hg}$ .
- s. Reduce  $\text{Bi}^{+++}$  to  $\text{Bi}$ .
- t. Oxidize  $\text{Sn}^{++}$  to  $\text{Sn}^{++++}$ .
- u. Dissolve  $\text{Cu}(\text{OH})_2$  but not  $\text{Bi}(\text{OH})_3$ .
- v. Oxidize  $\text{Cl}^-$  to  $\text{Cl}_2$ .

**16.** How would you distinguish between the following compounds by means of one reagent? (Tell what happens to each substance.)

a. *Solids:*

CuS and SnS	Cu(OH) <sub>2</sub> and Bi(OH) <sub>3</sub>
SnS <sub>2</sub> and As <sub>2</sub> S <sub>5</sub>	FeS and CdS
CdS and HgS	S and SnS <sub>2</sub>
PbSO <sub>4</sub> and Bi <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub>	SbCl <sub>3</sub> and PbCl <sub>2</sub>
Hg <sub>2</sub> Cl <sub>2</sub> and HgCl <sub>2</sub>	ZnS and CuS

b. *Solutions:*

(NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> and (NH <sub>4</sub> ) <sub>3</sub> SbS <sub>4</sub>	H <sub>2</sub> S and HCl
CdCl <sub>2</sub> and CuCl <sub>2</sub>	Na <sub>3</sub> AsO <sub>4</sub> and NaCl
Pb(NO <sub>3</sub> ) <sub>2</sub> and Cd(NO <sub>3</sub> ) <sub>2</sub>	SbCl <sub>3</sub> and AlCl <sub>3</sub>
SnCl <sub>2</sub> and HgCl <sub>2</sub>	(NH <sub>4</sub> ) <sub>2</sub> SnS <sub>3</sub> and SnCl <sub>2</sub>
HNO <sub>3</sub> and HCl	SnCl <sub>2</sub> and SbCl <sub>3</sub>
H <sub>2</sub> SO <sub>4</sub> and HNO <sub>3</sub>	H <sub>2</sub> SO <sub>4</sub> and HCl

**17.** A colorless copper-arsenic group unknown solution turned milky white when diluted with water but became colorless again when acidified with HCl. Explain.

**18.** A colorless solution which was known to contain only cations of the copper-arsenic group gave a dark-brown precipitate in the regular H<sub>2</sub>S precipitation. This precipitate was completely insoluble in (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub> and completely soluble in warm dilute HNO<sub>3</sub>. What conclusions can be drawn?

**19.** A mixture of solid chlorides, known to contain only metals of the copper-arsenic group, dissolved readily and completely in cold water to give a clear pale-blue solution. The regular H<sub>2</sub>S precipitation gave a brown precipitate. This precipitate was partially soluble in (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>; the residue, which did not dissolve in (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub>, was completely soluble in warm dilute HNO<sub>3</sub>. What conclusions can be drawn?

**20.** On being subjected to the regular H<sub>2</sub>S precipitation, a solution known to contain only cations of the copper-arsenic group gave an orange-yellow precipitate. What conclusions can be drawn?

**21.** A solution known to contain only cations of the copper-arsenic group was divided into four parts which were treated as described below:

a. One part, when diluted with water, gave a white precipitate; this precipitate dissolved on addition of HCl.

b. The second part gave no precipitate when warmed and treated with SnCl<sub>2</sub> solution.

c. The third part, on evaporation with H<sub>2</sub>SO<sub>4</sub> to white SO<sub>3</sub> fumes and dilution with water, gave a finely divided white precipitate.

d. The fourth part was treated with H<sub>2</sub>S in the usual manner. No precipitate was formed with H<sub>2</sub>S when the solution was hot and strongly acid, but on dilution with water a brownish black precipitate formed. This precipitate was partially soluble in (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub> at 60°. The decantate from the (NH<sub>4</sub>)<sub>2</sub>S<sub>2</sub> treatment, on being acidified with dilute HCl, gave a precipitate

which dissolved completely in 12N HCl. Sulfur was deposited in this reaction. What conclusions can be drawn?

**22.** The mixture of sulfides obtained when a copper-arsenic group unknown was completely precipitated with  $\text{H}_2\text{S}$  was completely insoluble in  $(\text{NH}_4)_2\text{S}_2$  and completely soluble in 3N  $\text{HNO}_3$ , sulfur being formed in the latter case. The solution obtained with  $\text{HNO}_3$  gave a colorless solution with no precipitate or milky suspension when treated with excess  $\text{NH}_4\text{OH}$ . What conclusions can be drawn?

## **Copper-arsenic group report**



## **Copper-arsenic group report**

## **Copper-arsenic group report**

## Copper-arsenic group report

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## **Copper-arsenic group report**

## **Copper-arsenic group report**

Solution containing  $\text{Al}^{+++}$ ,  $\text{Cr}^{+++}$ ,  $\text{Fe}^{+++}$ ,  $\text{Mn}^{++}$ ,  $\text{Zn}^{++}$ ,  $\text{Co}^{++}$ ,  $\text{Ni}^{++}$ ,  $\text{Ba}^{++}$ ,  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{Na}^{+}$ ,  $\text{K}^{+}$  and  $\text{NH}_4^{+}$



$\text{Al}(\text{OH})_3$ ,  $\text{Cr}(\text{OH})_3$ ,  $\text{Fe}(\text{OH})_3$ ,  $\text{Mn}^{++}$ ,  $\text{Zn}(\text{NH}_4)_4^{++}$ ,  $\text{Ni}(\text{NH}_4)_4^{++}$ ,  $\text{Co}(\text{NH}_4)_4^{++}$ ,  $\text{Ba}^{++}$ ,  $\text{Ca}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{Na}^{+}$ ,  $\text{K}^{+}$ ,  $\text{NH}_4^{+}$

$[\text{H}_2\text{S}]$  Proc. 15

$\text{Ca}^{++}$ ,  $\text{Ba}^{++}$ ,  $\text{Mg}^{++}$ ,  $\text{Na}^{+}$ ,  $\text{K}^{+}$ ,  $\text{NH}_4^{+}$   
Analyze according to Proc. 22

$\text{Al}(\text{OH})_3$ ,  $\text{Cr}(\text{OH})_3$ ,  $\text{Fe}(\text{OH})_3$ ,  $\text{ZnS}$ ,  $\text{MnS}$ ,  $\text{CoS}$ ,  $\text{NiS}$ ,  $\text{FeS}$   
 $[\text{HCl}, \text{HNO}_3]$  Proc. 16

$\text{Al}^{+++}$ ,  $\text{Cr}^{+++}$ ,  $\text{Fe}^{+++}$ ,  $\text{Zn}^{++}$ ,  $\text{Mn}^{++}$ ,  $\text{Co}^{++}$ ,  $\text{Ni}^{++}$

$[\text{NaOH}]$

$\text{Fe}(\text{OH})_3$ ,  $\text{Mn}(\text{OH})_2$ ,  $\text{Ni}(\text{OH})_2$ ,  $\text{Co}(\text{OH})_2$ ,  $\text{AlO}_2^{---}$ ,  $\text{CrO}_2^{---}$ ,  $\text{ZnO}_2^{---}$

$[\text{Na}_2\text{O}_2]$

$\text{Fe}(\text{OH})_3$ ,  $\text{Ni}(\text{OH})_2$ ,  $\text{Co}(\text{OH})_2$ ,  $\text{MnO}_2$   
 $[\text{HCl}]$  Proc. 17

$\text{AlO}_2^{---}$ ,  $\text{ZnO}_2^{---}$ ,  $\text{CrO}_2^{---}$

$[\text{HNO}_3]$  Proc. 20

$\text{Al}^{+++}$ ,  $\text{Zn}^{++}$ ,  $\text{Cr}_2\text{O}_7^{---}$

$[\text{NH}_4\text{Cl}, \text{NH}_4\text{OH}]$

$\text{Mn}^{++}$ ,  $\text{Ni}(\text{NH}_4)_4^{++}$ ,  $\text{Co}(\text{NH}_4)_4^{++}$

$[\text{HCl}]$  Proc. 17

$\text{Fe}^{+++}$

$[\text{KCN}]$

$[\text{K}_2\text{Fe}(\text{CN})_6]$

$\text{Fe}(\text{CNS})_2$  Red

$\text{Fe}(\text{Fe}(\text{CNS})_2)_2$  Blue

$\therefore \text{Fe}$  present

$\text{MnS}$ ,  $\text{NiS}$ ,  $\text{CoS}$

$[\text{Dil. HCl}]$

$\text{Ni}^{++}$ ,  $\text{Co}^{++}$

$[\text{NH}_4\text{OH}]$

$\text{Ni}(\text{NH}_4)_4^{++}$ ,  $\text{Co}(\text{NH}_4)_4^{++}$

$[\text{CH}_3\text{COONa}]$

$[\text{H}_2\text{C}_2\text{O}_4]$

$[\text{C}_6\text{H}_5\text{NOO}]$

$\text{C}_6\text{H}_5\text{NO}_2$

$\text{Co}(\text{C}_6\text{H}_5\text{NOO})_2$

Red

$\therefore \text{Ni}^{++}$  present

$\text{Mn}^{++}$

$[\text{NaOH}]$

$\text{Mn}(\text{OH})_2$

$[\text{HNO}_3]$

$\text{Mn}^{++}$

$[\text{NaBiO}_3]$

$\text{MnO}_4^{--}$

Violet

$\therefore \text{Mn}^{++}$  present

$\text{Al}(\text{OH})_3$

$[\text{HNO}_3]$

$\text{Al}^{+++}$

$[\text{NH}_4\text{OH}]$

$\therefore \text{Al}^{+++}$  present

$\text{CrO}_2^{---}$ ,  $\text{Zn}(\text{NH}_4)_4^{++}$

$[\text{H C}_2\text{H}_3\text{O}_2]$  Proc. 21

$\text{Cr}_2\text{O}_7^{---}$ ,  $\text{Zn}^{++}$

$[\text{BaCl}_2]$

$\text{BaCrO}_4$

$[\text{H}_2\text{S}]$

$\text{ZnS}$

White

$\text{HCl}$

$\text{Zn}^{++}$

$\therefore \text{Cr}^{+++}$  present  $\therefore \text{Zn}^{++}$  present

OUTLINE 4: ANALYSIS OF THE ALUMINUM-NICKEL GROUP

## CHAPTER 5

### The Aluminum-Nickel Group

THE ADDITION OF  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{OH}$ , and  $\text{H}_2\text{S}$  to a solution containing all the metallic ions not precipitated in the preceding groups results in the precipitation of aluminum, chromium, and iron III as hydroxides, and manganese, nickel, cobalt, iron II, and zinc as sulfides. Under these conditions the hydroxides and sulfides of calcium, barium, magnesium, potassium, and sodium are soluble. This solubility permits a separation of the cations of the aluminum-nickel group from those of the barium-magnesium group.

#### **Procedure 15: Precipitation of the aluminum-nickel group in the absence of phosphates and borates**

If the solution to be analyzed is an aluminum-nickel group "known" or "unknown" (see Schedule of Laboratory Work 5 and 6, page 7), follow (A) (see Note 1). If the decantate from the copper-arsenic group precipitation, Procedure 5, is to be analyzed, follow (B).

(A) Place 6 drops of the aluminum-nickel group "known" or "unknown" solution in a test tube (see Note 2). Add 4 drops of 2N  $\text{NH}_4\text{Cl}$ , mix thoroughly, then add 15N  $\text{NH}_4\text{OH}$ , dropwise, with constant stirring, until the solution is just alkaline. Then add one extra drop of 15N  $\text{NH}_4\text{OH}$  and 20 drops of hot water and mix thoroughly. Treat with  $\text{H}_2\text{S}$  for 20–30 seconds. When precipitation with  $\text{H}_2\text{S}$  is complete, wash down the sides of the tube with a few drops of cold water, centrifuge, and decant, saving the decantate for Procedure 22 (see Note 3). Wash the precipitate three times with 15–20-drop portions of hot water containing 3 or 4 drops of 2N  $\text{NH}_4\text{Cl}$  and analyze according to Procedure 16.

(B) Place the decantate from Procedure 5 in a casserole and evaporate down carefully to a volume of 8 to 10 drops. Transfer to a test tube, centrifuge, and decant into a small test tube, discarding the precipitate. Treat the decantate in the test tube as directed in the second sentence of Method (A).

### NOTES

1. If phosphates, borates, fluorides, oxalates, silicates, or tartrates are present in a solution to be analyzed and if this solution also contains calcium, barium, or magnesium as well as metals of the aluminum-nickel group, a special series of procedures, different from those presented in this chapter, must be used. However, since the combination of ions just mentioned is rare and will not ordinarily be encountered in solutions being analyzed, the average analysis is carried out most successfully by using a more general procedure of the type presented in this chapter.

Fluorides, oxalates, silicates, and tartrates are not among the anions discussed in this book; therefore, they will not be present in solutions ordinarily submitted for analysis in this course.

If an unknown solution to be analyzed does, in fact, contain the combination of ions listed at the beginning of this note, the student should be referred to the basic acetate method in one of the reference textbooks listed at the end of Chapter 2.

2. If the aluminum-nickel group unknown is issued in the form of a finely divided solid, proceed as follows: Place in a test tube as much of the solid as can be carried on  $\frac{1}{4}$  in. of the tip of the spatula. Add 3–4 drops of 6N HCl, warm gently, and then add 5–6 drops of hot water. Mix thoroughly and heat carefully until a clear solution is obtained, replenishing the water and acid if necessary. Proceed with the analysis of this solution as directed in the second sentence of Procedure 15A.

If the solid unknown is not finely divided when received, the entire sample should first be pulverized in a clean mortar.

3. If the substance being analyzed is an aluminum-nickel group "known" or "unknown," this decantate can be discarded.

4.  $\text{NH}_4\text{Cl}$  is added, in the precipitation of the aluminum-nickel group, to prevent the precipitation of magnesium as  $\text{Mg}(\text{OH})_2$ ; if  $\text{Mg}(\text{OH})_2$  were to precipitate, the subsequent analysis of the group would be more complicated; hence it is desirable to carry magnesium over to the next group.

$\text{Mg}(\text{OH})_2$  will precipitate if a solution contains enough  $\text{Mg}^{++}$  ions



and enough  $\text{OH}^-$  ions so that the two, when they combine, will give more than enough  $\text{Mg}(\text{OH})_2$  to form a saturated solution; the extra  $\text{Mg}(\text{OH})_2$ , over and above what will ordinarily dissolve in the solution, will precipitate.

Ammonium hydroxide is a weak base; it may be represented as ionizing according to Equation (a):



Even though ammonium hydroxide is a weak base, it ionizes to give enough  $\text{OH}^-$  ions to form a precipitate with the concentration of  $\text{Mg}^{++}$  present in the usual "known" or "unknown" solution. Therefore, when  $\text{NH}_4\text{OH}$  alone is added to a water solution of an unknown containing  $\text{Mg}^{++}$ ,  $\text{Mg}(\text{OH})_2$  is precipitated.

$\text{NH}_4\text{Cl}$  is a salt and hence a strong electrolyte. Consequently,  $\text{NH}_4\text{Cl}$  in solution provides an abundance of  $\text{NH}_4^+$  ions. If  $\text{NH}_4\text{Cl}$  is present in a solution also containing ammonium hydroxide, the  $\text{NH}_4^+$  ions from  $\text{NH}_4\text{Cl}$  will shift the equilibrium point in Equation (a) to the left. This shift will greatly reduce the concentration of  $\text{OH}^-$  ions and will give a condition represented by Equation (b):



There are not enough  $\text{OH}^-$  ions present in Equation (b) to form a precipitate of  $\text{Mg}(\text{OH})_2$  with the  $\text{Mg}^{++}$  ions present in the average solution. In other words,  $\text{NH}_4\text{Cl}$  prevents the precipitation of  $\text{Mg}(\text{OH})_2$  by  $\text{NH}_4\text{OH}$ .

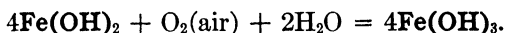
The decrease of the ionization of  $\text{NH}_4\text{OH}$  by ammonium ions from  $\text{NH}_4\text{Cl}$  is an example of the "common ion effect."  $\text{NH}_4\text{NO}_3$ ,  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$  or  $\text{NH}_4\text{Br}$  may be substituted for the  $\text{NH}_4\text{Cl}$ .

$\text{NH}_4\text{Cl}$  also prevents the precipitation of  $\text{Mn}(\text{OH})_2$  by  $\text{NH}_4\text{OH}$ , and in exactly the same way. However,  $\text{MnS}$  is quite insoluble, so that manganese precipitates as  $\text{MnS}$  when  $\text{H}_2\text{S}$  is added.  $\text{MgS}$  is soluble and does not precipitate.

The hydroxides of aluminum, chromium, and iron III are so insoluble that they precipitate even in the presence of the small amount of  $\text{OH}^-$  ions represented in Equation (b). The hydroxides of cobalt, nickel, and zinc are likewise so insoluble that they, too, will precipitate in the presence of the  $\text{OH}^-$  in Equation (b); they, however, redissolve in excess  $\text{NH}_4\text{OH}$  in a fashion to be discussed in Note 9.

The behavior of iron II in the presence of  $\text{NH}_4^+$  and  $\text{OH}^-$  is complicated by the fact that Fe II is readily oxidized by air to Fe III. The net result is that a green precipitate, probably  $\text{Fe}(\text{OH})_2 \cdot \text{Fe}(\text{OH})_3$ , is formed when  $\text{NH}_4\text{OH}$  is added to  $\text{Fe}^{++}$  even though

$\text{NH}_4\text{Cl}$  is present. This green precipitate gradually darkens as more  $\text{Fe}(\text{OH})_2$  is oxidized to  $\text{Fe}(\text{OH})_3$ :



5. The colors of the precipitates in this group are:

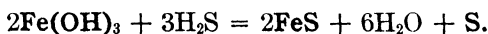
$\text{Fe}(\text{OH})_3$ .....	Brownish red	$\text{CoS}$ .....	Black
$\text{Cr}(\text{OH})_3$ .....	Grayish green	$\text{MnS}$ .....	Pink
$\text{Al}(\text{OH})_3$ .....	White	$\text{NiS}$ .....	Black
$\text{FeS}$ .....	Black	$\text{ZnS}$ .....	White

Careful observation of the colors of the precipitate formed, first when  $\text{NH}_4\text{OH}$  is added and later when  $\text{H}_2\text{S}$  is added, may give definite information about the presence or absence of certain ions.

If  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH}$  give no precipitate, then aluminum, chromium, and ferric ions are of course definitely absent; if a white precipitate forms, the presence of aluminum is indicated; a green precipitate indicates chromium and a brownish-red precipitate indicates iron.

If the addition of  $\text{H}_2\text{S}$  gives no further precipitation, cobalt, nickel, manganese, and zinc ions are absent. If a white precipitate is formed, zinc is probably present; manganese, which forms a pink sulfide, may be present; and cobalt and nickel, whose sulfides are black, are definitely absent in appreciable quantities.

The formation of a black precipitate on addition of  $\text{H}_2\text{S}$  may be due to the conversion of red  $\text{Fe}(\text{OH})_3$  to black  $\text{FeS}$  according to the following equation:



If  $\text{NH}_4\text{OH}$  and  $\text{H}_2\text{S}$  were added together instead of being added separately, the hydroxides and sulfides would immediately precipitate together; it would then obviously be impossible to make the observations of color noted above.

6. The decantate from the copper-arsenic group is boiled down before the aluminum-nickel group is precipitated, in order to drive off all  $\text{H}_2\text{S}$  and to precipitate any sulfides of the copper-arsenic group that may have gone into the filtrate. If the  $\text{H}_2\text{S}$  were not removed, the sulfides and hydroxides of the aluminum-nickel group would all precipitate together when  $\text{NH}_4\text{OH}$  was added. As a result the desirable valuable observation of colors of precipitates referred to in Note 5 could not be made.

7.  $\text{NH}_4\text{Cl}$ , being a strong electrolyte, helps coagulate any hydroxides or sulfides, thereby preventing them from becoming colloidal. Similarly, the addition of  $\text{NH}_4\text{Cl}$  to the washing water at various

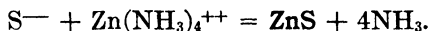
points in the analysis is for the purpose of preventing peptization and promoting coagulation and rapid settling.

8. A large excess of  $\text{NH}_4\text{OH}$  tends to peptize (cause to go colloidal)  $\text{NiS}$ ,  $\text{CoS}$ ,  $\text{Al}(\text{OH})_3$ ,  $\text{Cr}(\text{OH})_3$ , and  $\text{Fe}(\text{OH})_3$ , making them difficult to settle out. If a very large excess of  $\text{NH}_4\text{OH}$  has been added, the mixture should be boiled for one minute before centrifuging.

9. The behavior of zinc, nickel, and cobalt ions on being treated with  $\text{NH}_4\text{OH}$  is the same as that already noted for copper and cadmium ions (see Note 1, Procedure 9). The hydroxides of the three metals are first formed. Excess of  $\text{NH}_4\text{OH}$  dissolves these hydroxides with the formation of  $\text{Zn}(\text{NH}_3)_4^{++}$ ,  $\text{Ni}(\text{NH}_3)_4^{++}$ , and  $\text{Co}(\text{NH}_3)_6^{++}$ .

$\text{Zn}(\text{NH}_3)_4^{++}$  is colorless,  $\text{Ni}(\text{NH}_3)_4^{++}$  is pale blue, and  $\text{Co}(\text{NH}_3)_6^{++}$  has a characteristic deep reddish-brown color.

10. Hydrogen sulfide reacts with  $\text{Zn}(\text{NH}_3)_4^{++}$ ,  $\text{Ni}(\text{NH}_3)_4^{++}$ , and  $\text{Co}(\text{NH}_3)_6^{++}$  to form  $\text{ZnS}$ ,  $\text{NiS}$ , and  $\text{CoS}$  as follows:

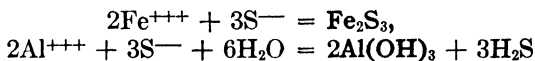


$\text{MnS}$  and  $\text{FeS}$  are formed by direct combination of the two ions involved:

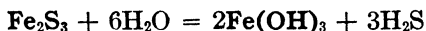


$\text{FeS}$  may also be formed by reduction of  $\text{Fe III}$  as mentioned in Note 5.

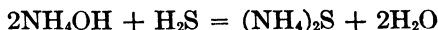
11. If  $(\text{NH}_4)_2\text{S}$  is added to a cold neutral solution containing aluminum, chromium, and ferric ions,  $\text{Al}(\text{OH})_3$ ,  $\text{Cr}(\text{OH})_3$ , and  $\text{Fe}_2\text{S}_3$  will be precipitated:



At higher temperatures  $\text{Fe}_2\text{S}_3$  is hydrolyzed, brownish-red  $\text{Fe}(\text{OH})_3$  being precipitated:



12. The concentration of sulfide ions would be very high in a solution formed by passing  $\text{H}_2\text{S}$  into a solution of  $\text{NH}_4\text{OH}$ . This high concentration of sulfide ions results from the fact that the  $(\text{NH}_4)_2\text{S}$  formed in the reaction



is a salt and is, accordingly, completely ionized into  $\text{NH}_4^+$  and  $\text{S}^{--}$ .

This high concentration of  $\text{S}^{--}$  results in very complete precipitation of zinc, manganese, cobalt, and nickel as sulfides.

## SEPARATION OF THE ALUMINUM GROUP FROM THE NICKEL GROUP

The hydroxides of aluminum, chromium, and zinc are amphoteric and are therefore soluble in NaOH. In contrast, the hydroxides of iron, manganese, cobalt, and nickel are not amphoteric; they are not soluble in NaOH. Upon this fact is based the separation of the cations of the aluminum group ( $\text{Al}^{+++}$ ,  $\text{Cr}^{+++}$ , and  $\text{Zn}^{++}$ ) from the cations of the nickel group ( $\text{Fe}^{+++}$ ,  $\text{Mn}^{++}$ ,  $\text{Co}^{++}$ , and  $\text{Ni}^{++}$ ).

### Procedure 16: Separation of the aluminum group from the nickel group

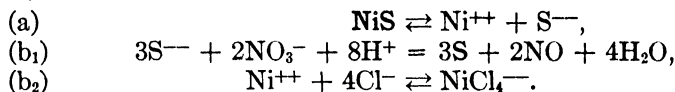
Treat the precipitate from Procedure 15 with 10 drops of 12N HCl, mix thoroughly, and boil gently for half a minute. If the precipitate is not completely dissolved, add 3 drops of 16N  $\text{HNO}_3$ , mix thoroughly, and boil gently until a clear solution is obtained. Add 10 drops of cold water, centrifuge to remove any precipitate of sulfur, and decant into a casserole. Make the solution just alkaline with 8N NaOH; then add  $\text{Na}_2\text{O}_2$ , a little at a time (see Note 1) with constant stirring, until a quantity half the size of an average drop of water from a medicine dropper has been added. When the reaction of the  $\text{Na}_2\text{O}_2$  begins to slow down, boil gently for about half a minute. Transfer the solution to a test tube before the precipitate has had a chance to settle, and centrifuge. Decant carefully, saving the decantate for Procedure 20. Wash the precipitate three times with hot water and analyze according to Procedure 17.

### NOTES

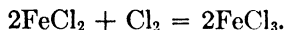
1. The solid sodium peroxide ( $\text{Na}_2\text{O}_2$ ) is added by means of a small metal spatula. Since it is highly corrosive, great care should be taken to avoid having it come in contact with any part of the body.

2.  $\text{Al}(\text{OH})_3$ ,  $\text{Fe}(\text{OH})_3$ ,  $\text{Cr}(\text{OH})_3$ ,  $\text{MnS}$ ,  $\text{FeS}$ , and  $\text{ZnS}$  are readily soluble in HCl.  $\text{NiS}$  and  $\text{CoS}$  are not readily soluble in HCl but are

soluble in aqua regia ( $\text{HCl} + \text{HNO}_3$ ). (See Notes 3 and 5, Procedure 7.)



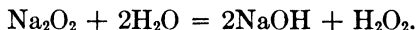
Aqua regia oxidizes Fe II to Fe III:



3. When NaOH is added to a solution containing the members of the aluminum-nickel group, the hydroxides of all seven metals are first precipitated. The hydroxides of aluminum, chromium, and zinc are amphoteric (see Note 4, Procedure 9) and dissolve in an excess of NaOH to form  $\text{Na}_3\text{AlO}_3$ ,  $\text{Na}_2\text{CrO}_3$ , and  $\text{Na}_2\text{ZnO}_2$ , respectively. The hydroxides of iron, manganese, cobalt, and nickel are not amphoteric and do not dissolve in excess of NaOH.

<i>Solution</i>	<i>Precipitate</i>	<i>Solution</i>
$\text{Al}^{+++}$	$\text{Al}(\text{OH})_3$	$\text{Na}_3\text{AlO}_3$
$\text{Cr}^{+++}$	$\text{Cr}(\text{OH})_3$	$\text{Na}_2\text{CrO}_3$
$\text{Zn}^{++}$	$\text{Zn}(\text{OH})_2$	$\text{Na}_2\text{ZnO}_2$
$\text{Fe}^{+++} + \text{NaOH} = \text{Fe}(\text{OH})_3 + \text{excess NaOH} =$		
$\text{Mn}^{++}$	$\text{Mn}(\text{OH})_2$	<i>Residue</i>
$\text{Ni}^{++}$	$\text{Ni}(\text{OH})_2$	$\text{Fe}(\text{OH})_3$
$\text{Co}^{++}$	$\text{Co}(\text{OH})_2$	$\text{Mn}(\text{OH})_2$
		$\text{Ni}(\text{OH})_2$
		$\text{Co}(\text{OH})_2$

4. Sodium peroxide is added to oxidize  $\text{Na}_2\text{CrO}_3$  to  $\text{Na}_2\text{CrO}_4$  for the reason discussed in Note 1, Procedure 20. Sodium peroxide first reacts with water to form  $\text{H}_2\text{O}_2$ :

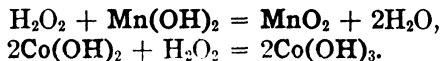


The  $\text{H}_2\text{O}_2$  then oxidizes  $\text{CrO}_3^{--}$  to  $\text{CrO}_4^{--}$  as follows:



$\text{CrO}_3^{--}$  is pale green;  $\text{CrO}_4^{--}$  is yellow. Therefore if the color of the solution changes from pale green to yellow on treatment with  $\text{Na}_2\text{O}_2$ , chromium is present.

5. Hydrogen peroxide oxidizes  $\text{Mn}(\text{OH})_2$  to  $\text{MnO}_2$  and  $\text{Co}(\text{OH})_2$  to  $\text{Co}(\text{OH})_3$  as follows:



$\text{MnO}_2$  and  $\text{Co(OH)}_3$  are black. Hence a darkening of the color of the precipitated hydroxides on addition of  $\text{Na}_2\text{O}_2$  may indicate the presence of manganese or cobalt.

6. When  $\text{Na}_2\text{O}_2$  reacts with water, a great deal of heat is liberated. This heat decomposes the  $\text{H}_2\text{O}_2$ :



If the rate of addition of  $\text{Na}_2\text{O}_2$  is too rapid, the solution may "boil" right out of the container.

7. Any excess  $\text{Na}_2\text{O}_2$  or  $\text{H}_2\text{O}_2$  present in the solution must be decomposed by boiling; otherwise it will interfere with the subsequent analysis as discussed in Note 3, Procedure 20.

8. A careful observation of colors of solutions and precipitates formed in Procedure 16 may give valuable information regarding the cations present. The colors are:

$\text{AlCl}_3$ .....	Colorless	$\text{Ni(OH)}_2$ .....	Green
$\text{ZnCl}_2$ .....	Colorless	$\text{Mn(OH)}_2$ .....	White or pale pink
$\text{MnCl}_2$ .....	Colorless to faint pink	$\text{Co(OH)}_2$ .....	Pink
$\text{FeCl}_3$ .....	Reddish brown to yellow	$\text{MnO}_2$ .....	Black or dark brown
$\text{CrCl}_3$ .....	Green	$\text{Co(OH)}_3$ .....	Black
$\text{NiCl}_2$ .....	Green		
$\text{CoCl}_2$ .....	Reddish pink		

Pure freshly precipitated  $\text{Mn(OH)}_2$  is white, but it rapidly turns brown in contact with air because of oxidation to  $\text{MnO}_2$  and  $\text{Mn}_2\text{O}_3$ .

The precipitate formed when  $\text{NaOH}$  is added to  $\text{Co}^{++}$  may vary in color from blue to pink to light brown.  $\text{Co(OH)}_2$  is pink. The pink color is not always obtained because  $\text{NaOH}$  may form the blue basic salt,  $\text{Co(OH)Cl}$ . This becomes pink  $[\text{Co(OH)}_2]$  on heating. The pink hydroxide may be oxidized by the air to form black  $\text{Co(OH)}_3$ .

A pink  $\text{CoCl}_2$  solution turns blue when heated to boiling but regains its pink color when cooled. A pink solution of  $\text{CoCl}_2$  turns blue when treated with concentrated  $\text{HCl}$ ; the pink color is restored by dilution with water. These color changes are due to changes in the composition and structure of the complex ions present in the solution. The pink color is due to the  $\text{Co(H}_2\text{O)}_6^{++}$  ion; the blue color is due to the  $\text{CoH}_2\text{OCl}_3^-$  and  $\text{CoCl}_4^-$  ions.

9. *Unused  $\text{Na}_2\text{O}_2$  should not be thrown into waste jars; it should be placed in the sink and flushed away with plenty of water. If thrown into waste jars containing paper or other combustible material it may start a fire because of its violent oxidizing nature.*

## SEPARATION OF IRON FROM MANGANESE, NICKEL, AND COBALT

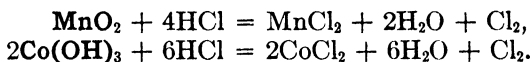
When  $\text{NH}_4\text{Cl}$  and excess  $\text{NH}_4\text{OH}$  are added to a solution containing iron III, manganese, nickel, and cobalt ions the iron is precipitated as  $\text{Fe}(\text{OH})_3$  leaving  $\text{Mn}^{++}$ ,  $\text{Ni}(\text{NH}_3)_4^{++}$  and  $\text{Co}(\text{NH}_3)_6^{++}$  in solution.

### Procedure 17: Separation and detection of iron

Treat the precipitate from Procedure 16 with 10 drops of 12N  $\text{HCl}$ , mix thoroughly, and heat carefully until completely dissolved. Add 10 drops of 2N  $\text{NH}_4\text{Cl}$ , and then add 15N  $\text{NH}_4\text{OH}$ , with constant stirring, until the solution is alkaline. Then add a 2-drop excess of 15N  $\text{NH}_4\text{OH}$ . Mix thoroughly, centrifuge at once, and decant immediately into a test tube, saving this decantate for Procedure 18. Wash the precipitate three times with hot water; then dissolve it in 4–6 drops of 1.5N  $\text{HCl}$  and dilute with 10 drops of water. Divide the solution into two parts. To one part add a drop of N  $\text{K}_4\text{Fe}(\text{CN})_6$ . A blue precipitate ( $\text{Fe}_4(\text{Fe}(\text{CN})_6)_3$ ) proves the presence of iron. To the second part add N  $\text{KCNS}$  or  $\text{NH}_4\text{CNS}$ . A red color  $[\text{Fe}(\text{CNS})_6]^{---}$  proves the presence of iron.

### NOTES

1.  $\text{MnO}_2$ , and  $\text{Co}(\text{OH})_3$  are insoluble in  $\text{HNO}_3$  but dissolve in  $\text{HCl}$  as follows:



$\text{Ni}(\text{OH})_2$  and  $\text{Fe}(\text{OH})_3$  dissolve readily in  $\text{HCl}$  to give  $\text{NiCl}_2$  and  $\text{FeCl}_3$ , respectively.

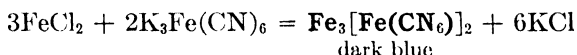
2.  $\text{NH}_4\text{Cl}$  prevents the precipitation of  $\text{Mn}(\text{OH})_2$  by  $\text{NH}_4\text{OH}$ , as explained in Note 4, Procedure 15. However, a precipitate gradually forms if the solution is allowed to stand in contact with air. This precipitate is a mixture of brown  $\text{Mn}_2\text{O}_3$  and black  $\text{MnO}_2$  formed when  $\text{Mn}^{++}$  is oxidized by the air. To prevent this precipitation, with resulting loss of manganese, the solution is centrifuged and decanted as quickly as possible. Any  $\text{Mn}_2\text{O}_3$  and  $\text{MnO}_2$  that precipitate out

will not interfere seriously with the confirmatory test for iron.

3. The confirmatory tests for iron are both very delicate, so delicate in fact that iron should not be reported unless both tests are strong.

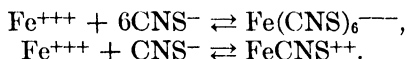
Traces of iron are often introduced as impurities in the course of the manufacture of the compounds used in making up the unknown and compounds used as reagents in the analysis. Hence, the student should learn to distinguish between a weak test which indicates a trace of iron, probably as an impurity, and a strong positive test. In case of doubt, tests for iron II and iron III should be made on the original sample (see Note 4).

4. To test for iron in a mixture, proceed as follows: Dissolve a small sample of the solid in 10–15 drops of dilute HCl. Divide the solution into three parts. Test two parts for iron III ions according to Procedure 17. To the third part, add a few drops of potassium ferricyanide ( $\text{K}_3\text{Fe}(\text{CN})_6$ ). A dark-blue precipitate (Turnbull's blue) proves the presence of  $\text{Fe}^{++}$  ions:



Note particularly that whereas potassium ferrocyanide ( $\text{K}_4\text{Fe}(\text{CN})_6$ ) gives a dark-blue precipitate with  $\text{Fe}^{+++}$ , potassium ferricyanide ( $\text{K}_3\text{Fe}(\text{CN})_6$ ) gives a dark-blue precipitate with  $\text{Fe}^{++}$ .

5. There is still some question as to what produces the red color in the test for  $\text{Fe}^{+++}$ . Although the  $\text{Fe}(\text{CNS})_6^{---}$  ion is widely accepted as the colored substance, there is evidence that  $\text{FeCNS}^{++}$  may be the colored ion:



### SEPARATION OF MANGANESE FROM COBALT AND NICKEL

The separation of manganese from cobalt and nickel depends on the fact that when the sulfides of these three metals are treated with cold dilute HCl,  $\text{MnS}$  is dissolved immediately, whereas  $\text{CoS}$  and  $\text{NiS}$  are only very slightly affected.

#### Procedure 18: Separation of manganese from cobalt and nickel and detection of manganese

Treat the decantate from Procedure 17 with  $\text{H}_2\text{S}$  for 20–30 seconds. Centrifuge and decant, discarding the decantate.



Wash the precipitate three times with hot water to which 5 drops of 2N  $\text{NH}_4\text{Cl}$  have been added. Add 10 drops of 1.5N  $\text{HCl}$  to this precipitate and stir for one minute. Centrifuge, and draw off the supernatant liquid with a medicine dropper; save this decantate for the detection of manganese. Wash the precipitate once with 3N  $\text{HCl}$  (5 drops of water plus 5 drops of 6N  $\text{HCl}$ ) and twice with hot water and save for Procedure 19.

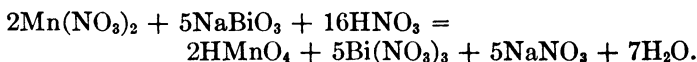
**Detection of manganese.** Boil the decantate, saved for the detection of manganese, gently for about half a minute, cool, make just alkaline with 8N  $\text{NaOH}$ , and then add an excess of 1 drop of  $\text{NaOH}$ . Centrifuge and decant, discarding the decantate, and wash the precipitate three times with hot water. Treat this precipitate with 5–6 drops of 3N  $\text{HNO}_3$  and a quantity of sodium bismuthate ( $\text{NaBiO}_3$ ) about one-fourth the size of a drop of water from a medicine dropper. Mix thoroughly. A purple-pink solution due to the presence of permanganate ( $\text{MnO}_4^-$ ) proves the presence of manganese.

#### NOTES

1. In the separation of  $\text{MnS}$  from  $\text{CoS}$  and  $\text{NiS}$ , small amounts of  $\text{CoS}$  and  $\text{NiS}$  may dissolve. These small amounts of  $\text{Co}^{++}$  and  $\text{Ni}^{++}$  do not, however, interfere with the test for manganese. If appreciable amounts of  $\text{CoS}$  dissolve, the pink color of cobalt nitrate may be mistaken for the violet of  $\text{MnO}_4^-$ .

2. The fact that nickel and cobalt do not precipitate in the copper-arsenic group indicates that  $\text{NiS}$  and  $\text{CoS}$  are soluble in dilute  $\text{HCl}$ . However, in the analysis of the aluminum-nickel group  $\text{CoS}$  and  $\text{NiS}$  do not dissolve in either dilute or concentrated  $\text{HCl}$ . This contradictory behavior is explained as follows: Freshly precipitated  $\text{NiS}$  and  $\text{CoS}$  exist in a form readily dissolved by dilute  $\text{HCl}$ . On standing, this soluble modification changes into a second form which is insoluble in both dilute and concentrated  $\text{HCl}$ .

3. The oxidation of  $\text{Mn}^{++}$  to  $\text{MnO}_4^-$  by sodium bismuthate ( $\text{NaBiO}_3$ ) takes place as follows:



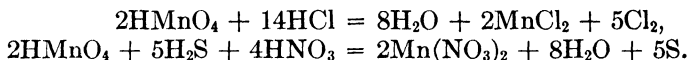
4. Reducing agents of any kind, such as chlorides and sulfides, will

interfere with the confirmatory test for manganese because they reduce the violet  $\text{MnO}_4^-$ , destroying its color. For that reason,

(a) The filtrate containing manganese ions is boiled to drive off all  $\text{H}_2\text{S}$ .

(b) Manganese is precipitated as  $\text{Mn}(\text{OH})_2$  and the precipitate of  $\text{Mn}(\text{OH})_2$  is washed free from chlorides.

Permanganic acid is reduced by chlorides and sulfides as follows:



5. The formation of  $\text{MnO}_4^-$  is a very delicate test for  $\text{Mn}^{++}$ . The test may be carried out on a sample of the original solid as follows: Boil a pinch of the solid material with  $\text{HCl}$ . Filter. Precipitate the  $\text{Mn}(\text{OH})_2$  with excess  $\text{NaOH}$  and test the carefully washed precipitate for manganese as directed in Procedure 18. Cobalt interferes with this test.

6. Bismuth is predominantly metallic in character; its common valence is 3 and its compounds ionize to give  $\text{Bi}^{+++}$  ions. In the compound  $\text{NaBiO}_3$ , bismuth has a valence of 5 and has the property of a nonmetal in that it is present in the negative ion  $\text{BiO}_3^-$ . This behavior of bismuth illustrates the rule that as the valence of a polyvalent element increases it becomes more nonmetallic in character.

7. The behavior of  $\text{NaBiO}_3$  illustrates the rule that the higher valenced compounds of polyvalent elements very generally can act as oxidizing agents. Other compounds (oxidizing agents) that illustrate this rule are  $\text{KMnO}_4$ ,  $\text{K}_2\text{Cr}_2\text{O}_7$ ,  $\text{KClO}_3$ , and  $\text{KIO}_4$ .

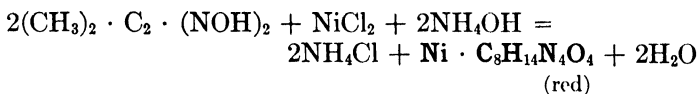
### Procedure 19: Detection of nickel and cobalt

Treat the precipitate from Procedure 18 with 10 drops of 12N  $\text{HCl}$  and 3 drops of 16N  $\text{HNO}_3$ , mix thoroughly, and heat gently until a clear solution is obtained. Add 6 drops of water, mix well, centrifuge, and decant into a test tube, discarding the precipitate (S). Make the decantate alkaline with 15N  $\text{NH}_4\text{OH}$  and divide it into two parts. To one part add 4–8 drops of dimethyl glyoxime. A yellowish-red precipitate ( $\text{NiC}_8\text{H}_{14}\text{N}_4\text{O}_4$ ) proves the presence of nickel. Make the second part acid with 5N  $\text{HC}_2\text{H}_3\text{O}_2$  (see Note 5). Then add 4–8 drops of  $\alpha$ -nitroso- $\beta$ -naphthol. A brownish-red precipitate [ $\text{Co}(\text{C}_{10}\text{H}_6\text{NO}_2)_3$ ], which may form slowly, proves the presence of cobalt.

## NOTES

1. As in the case of the difficultly soluble  $\text{HgS}$ ,  $\text{NiS}$ , and  $\text{CoS}$  are dissolved by means of reagents which liberate chlorine.

2. The following reaction takes place in the confirmatory test for nickel:

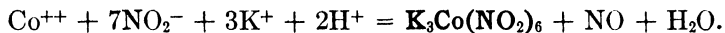


Since the red compound is readily soluble in acids, the reaction must be carried out in alkaline solution. Cobalt does not interfere with this test. Iron II ions react with  $(\text{CH}_3)_2\text{C}_2(\text{NOH})_2$  to form a soluble red compound; however, no precipitate is formed.

3. The formation of the dark-red cobaltinitroso- $\beta$ -naphthol  $[\text{Co}(\text{C}_{10}\text{H}_6\text{NO} \cdot \text{O})_3]$  is a very delicate test for cobalt. The equation for the reaction involved is very complex,  $\text{Co}^{++}$  being oxidized to  $\text{Co}^{+++}$ .

4. Because of the striking similarity in the chemical behavior of cobalt and nickel, their separation offers considerable difficulty. It is most convenient to test for them in the presence of each other in the manner outlined above.

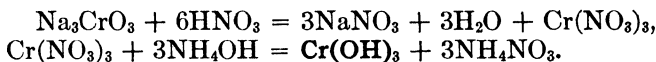
5. Cobalt may be identified as follows: Treat 3 drops of the solution which has been acidified with  $\text{HC}_2\text{H}_3\text{O}_2$  with 3 drops of  $\text{N KNO}_2$ . Warm, and allow to stand 10–20 minutes. A yellow precipitate  $[\text{K}_3\text{Co}(\text{NO}_2)_6]$  proves the presence of cobalt:

**Procedure 20: Separation and detection of aluminum**

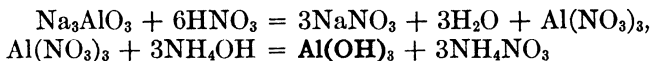
Treat the decantate from Procedure 16 with 16N  $\text{HNO}_3$  until slightly acid, then add 15N  $\text{NH}_4\text{OH}$  until distinctly alkaline; continue the stirring of the solution for 1 minute. Centrifuge and decant, saving the decantate for Procedure 21. Wash the precipitate three times with hot water, then dissolve it in 4–5 drops of 3N  $\text{HNO}_3$ . (If any precipitate fails to dissolve, remove it by centrifuging and decantation.) Make the solution alkaline with 15N  $\text{NH}_4\text{OH}$ . A white flocculent precipitate  $[\text{Al}(\text{OH})_3]$  proves the presence of aluminum.

## NOTES

1. It is imperative that  $\text{Na}_3\text{CrO}_3$  be completely oxidized to  $\text{Na}_2\text{CrO}_4$  in Procedure 16. Any unoxidized  $\text{Na}_3\text{CrO}_3$  would react as follows in Procedure 20:

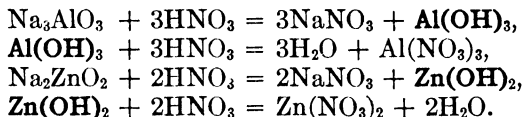


Sodium aluminate ( $\text{Na}_3\text{AlO}_3$ ) undergoes the same sort of reaction:

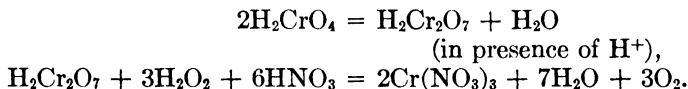


It is thus evident that if  $\text{Na}_3\text{CrO}_3$  were not oxidized to  $\text{Na}_2\text{CrO}_4$ ,  $\text{Cr}(\text{OH})_3$  would precipitate when the test for aluminum was made.  $\text{Cr}(\text{OH})_3$  is green, but in small amounts the color is not marked, and the  $\text{Cr}(\text{OH})_3$  precipitate may be mistaken for  $\text{Al}(\text{OH})_3$ .

2. When  $\text{HNO}_3$  is added in the first step in Procedure 20, a precipitate sometimes forms when the solution is just about neutral and then redissolves when more  $\text{HNO}_3$  is added. This precipitate may be either  $\text{Al}(\text{OH})_3$  or  $\text{Zn}(\text{OH})_2$ . The reactions involved are



3. Excess  $\text{Na}_2\text{O}_2$  and  $\text{H}_2\text{O}_2$ , if present in the decantate from Procedure 16, will interfere with the separation and identification of aluminum and chromium. When  $\text{HNO}_3$  is added in the first step in Procedure 20, the following reactions will take place:

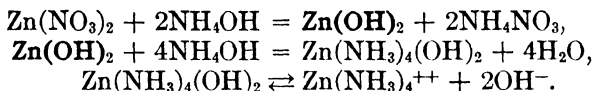


The chromate is thus reduced to  $\text{Cr}^{+++}$ . This  $\text{Cr}^{+++}$  will then interfere with the test for aluminum, as already discussed in Note 1.

Compare the above equation with the equation given in Note 4, Procedure 16. In alkaline solution the  $\text{H}_2\text{O}_2$  oxidizes trivalent chromium to chromate, whereas in strongly acid solution it reduces chromate to trivalent chromium.

4. If a green precipitate ( $\text{Cr}(\text{OH})_3$ ) appears when  $\text{NH}_4\text{OH}$  is added in Procedure 20, wash the precipitate and reanalyze it, starting with Procedure 16.

5. When  $\text{NH}_4\text{OH}$  is added to precipitate  $\text{Al}(\text{OH})_3$  in Procedure 20, a white precipitate sometimes forms which redissolves when more  $\text{NH}_4\text{OH}$  is added. This precipitate is probably  $\text{Zn}(\text{OH})_2$ . The reactions involved are



6. Since  $\text{HCl}$  may reduce chromate to  $\text{Cr}^{+++}$ , the solution is acidified with  $\text{HNO}_3$  rather than with  $\text{HCl}$ .

7. If lead, tin, and antimony are not completely precipitated in the copper-arsenic group, they appear as insoluble hydroxides or basic salts in the final test for aluminum. The hydroxides of lead, tin, and antimony, like  $\text{Al}(\text{OH})_3$ , are amphoteric. Also, their hydroxides, like  $\text{Al}(\text{OH})_3$ , do not dissolve in excess  $\text{NH}_4\text{OH}$ .

### Procedure 21: Separation and detection of chromium and zinc

Follow (A) if the decantate from Procedure 20 is colorless; follow (B) if it is yellow.

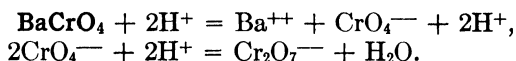
(A) *Decantate is colorless; therefore chromium is absent.* Make the decantate just acid with 5N  $\text{HC}_2\text{H}_3\text{O}_2$ . Treat with  $\text{H}_2\text{S}$  for 10–20 seconds. A white precipitate (**ZnS**) proves the presence of zinc.

(B) *Decantate is yellow; chromium is probably present.* Make the yellow decantate just slightly acid with 5N  $\text{HC}_2\text{H}_3\text{O}_2$ , add 6–7 drops of N  $\text{BaCl}_2$ , mix thoroughly, centrifuge until the supernatant liquid is clear, and decant, saving the decantate for Part (C) below. Wash the precipitate ( $\text{BaCrO}_4$ , mixed with some  $\text{BaSO}_4$ ) twice with hot water, add 3 drops of 3N  $\text{HNO}_3$  and stir for about 10 seconds. Add 10 drops of cold water, mix thoroughly, and then add 5 drops of ether and 1 drop of 3 per cent  $\text{H}_2\text{O}_2$  and shake. A blue coloration of the ether layer due to chromium peroxide ( $\text{CrO}_5$ ) proves the presence of chromium.

(C) Treat the decantate from (B) with  $\text{H}_2\text{S}$  for 10–20 seconds. A white precipitate (**ZnS**) which dissolves readily in 6N  $\text{HCl}$  proves the presence of zinc.

## NOTES

1. The final test for chromium depends on the fact that in dilute acid solution  $\text{Cr}_2\text{O}_7^{--}$  is oxidized by  $\text{H}_2\text{O}_2$  to form a deep indigo-blue compound, chromium peroxide,  $\text{CrO}_5$ . Yellow chromate is first changed to orange dichromate ( $\text{Cr}_2\text{O}_7^{--}$ ):

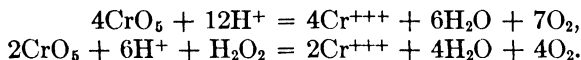


This change of chromate to dichromate, which always takes place when the solution is acidified, has already been referred to in Note 3, Procedure 20.

The dichromate is then converted to  $\text{CrO}_5$  by  $\text{H}_2\text{O}_2$ :



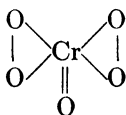
The compound,  $\text{CrO}_5$ , is unstable, and decomposes on standing to form  $\text{Cr}^{+++}$ . If the concentration of  $\text{HNO}_3$  is low, the  $\text{CrO}_5$  decomposes very slowly; if, however, the concentration of  $\text{HNO}_3$  is high, it decomposes so rapidly that the blue color may not be noticed. Furthermore,  $\text{CrO}_5$  is very rapidly reduced to  $\text{Cr}^{+++}$  by excess  $\text{H}_2\text{O}_2$ . Hence, high concentrations of  $\text{HNO}_3$  and excess  $\text{H}_2\text{O}_2$  must be avoided.



$\text{CrO}_5$  is very soluble in ether;  $\text{HNO}_3$  is not. Shaking with ether partially separates the  $\text{CrO}_5$  from the  $\text{HNO}_3$  and concentrates it in the ether layer. Since separation from  $\text{HNO}_3$  will increase its stability, shaking with ether preserves as well as concentrates the  $\text{CrO}_5$ .

The exact composition of the blue substance formed in the confirmatory test for chromium has been, and still is, the subject of much research, speculation, and controversy. That the composition is correctly represented by the formula  $\text{CrO}_5$  seems pretty well proved. Other formulas that have been suggested are  $\text{HCrO}_4$ ,  $\text{HCrO}_5$ ,  $\text{H}_2\text{CrO}_5$ ,  $\text{H}_2\text{CrO}_6$ ,  $\text{H}_3\text{CrO}_8$ , and  $\text{H}_6\text{Cr}_2\text{O}_{16}$ .

The following structure has been proposed for  $\text{CrO}_5$ . Note that chromium has a valence of 6, the same as in  $\text{CrO}_4^{--}$  or  $\text{Cr}_2\text{O}_7^{--}$ .



2. Before the addition of  $\text{BaCl}_2$  in the precipitation of the chromate as  $\text{BaCrO}_4$ , the solution is acidified with acetic acid rather than  $\text{HCl}$  or  $\text{HNO}_3$  because  $\text{BaCrO}_4$ , being the insoluble salt of a weak acid, is insoluble in a weak acid, such as acetic, but is soluble in a strong acid, such as  $\text{HCl}$  or  $\text{HNO}_3$ .

3. The precipitate obtained on addition of  $\text{BaCl}_2$  may contain varying amounts of  $\text{BaSO}_4$  because of oxidation of  $\text{H}_2\text{S}$  and  $\text{S}$  to  $\text{H}_2\text{SO}_4$  in earlier procedures.  $\text{BaSO}_4$  is white, whereas  $\text{BaCrO}_4$  is light yellow.  $\text{BaSO}_4$  is insoluble in  $\text{HNO}_3$ .

4. All  $\text{CrO}_4^{2-}$  must be precipitated before the confirmatory test for zinc is made.  $\text{CrO}_4^{2-}$ , if present, oxidizes  $\text{H}_2\text{S}$ , liberating sulfur. This finely divided sulfur, being white, would mask the white precipitate of  $\text{ZnS}$ .

### Questions

1. Using the scheme of analysis as a guide, write equations for all reactions that take place in the precipitation and analysis of the aluminum-nickel group.

2. Upon what fact or facts is each of the following based?

a. The separation of the cations of the aluminum-nickel group from the cations of the barium-magnesium group.

b. The separation of the aluminum group from the nickel group.

c. The separation of iron from manganese, cobalt, and nickel.

d. The separation of manganese from cobalt and nickel.

e. The separation of aluminum from chromium and zinc.

f. The separation of chromium from zinc.

3. Give the reason or reasons for each of the following:

a. Evaporating the decantate from the copper-arsenic group precipitation down to 10 drops and centrifuging before precipitating the aluminum-nickel group.

b. The addition of  $\text{NH}_4\text{Cl}$  before precipitating the aluminum-nickel group.

c. The separate addition, first, of  $\text{NH}_4\text{OH}$ , then of  $\text{H}_2\text{S}$ , in the precipitation of the aluminum-nickel group.

d. Avoiding a large excess of  $\text{NH}_4\text{OH}$  in the precipitation of the aluminum-nickel group.

e. The separate addition of  $\text{HCl}$  and  $\text{HNO}_3$ , followed in each case by boiling, in dissolving the aluminum-nickel group precipitate (Procedure 16).

f. The slow and careful addition of  $\text{Na}_2\text{O}_2$  (Procedure 16).

g. Boiling the solution before centrifuging in the separation of the aluminum group from the nickel group (Procedure 16).

h. Centrifuging off the  $\text{Fe}(\text{OH})_3$  immediately in the separation of iron from manganese, cobalt, and nickel (Procedure 17).

i. Complete removal of  $\text{H}_2\text{S}$  and chlorides before making the confirmatory test for manganese.

j. The use of dilute  $\text{HNO}_3$  rather than concentrated  $\text{HNO}_3$  in the confirmatory test for chromium.

k. The use of ether in the confirmatory test for chromium.

4. In the precipitation and analysis of the aluminum-nickel group, what difficulties, if any, would arise under the following conditions?

a. If  $\text{Na}_2\text{CrO}_3$  were not completely oxidized to  $\text{Na}_2\text{CrO}_4$  (Procedure 16).

b. If excess  $\text{Na}_2\text{O}_2$  and  $\text{H}_2\text{O}_2$  were not decomposed (Procedure 16).

c. If unused  $\text{Na}_2\text{O}_2$  were dumped into waste jars containing paper.

d. If 1 cc. of  $\text{H}_2\text{O}_2$  were used instead of 1 drop in the confirmatory test for chromium.

5. Write an equation or equations for a reaction occurring in the precipitation and analysis of the aluminum-nickel group in which:

a.  $\text{Fe}^{++}$  is oxidized to  $\text{Fe}^{+++}$ .

b.  $\text{Mn}^{++}$  is oxidized to  $\text{Mn}^{++++}$ .

c.  $\text{Mn}^{++}$  is oxidized to  $\text{MnO}_4^-$ .

d.  $\text{Mn}^{++++}$  is reduced to  $\text{Mn}^{++}$ .

e. Manganese is reduced from +7 to +2.

f. Chromium is oxidized from +3 to +6.

g. Sulfur is oxidized from -2 to 0.

h.  $\text{CrO}_5$  is reduced to  $\text{Cr}^{+++}$ .

i.  $\text{Cr}_2\text{O}_7^{--}$  is reduced to  $\text{Cr}^{+++}$ .

j.  $\text{CrO}_4^{--}$  is converted into  $\text{Cr}_2\text{O}_7^{--}$ .

k. Bismuth is reduced from +5 to +3.

l.  $\text{Al}(\text{OH})_3$  reacts amphoteric.

m.  $\text{ZnO}_2^{--}$  is converted into  $\text{Zn}^{++}$ .

n.  $\text{Cr}^{+++}$  is converted into  $\text{CrO}_3^{--}$ .

o.  $\text{Ni}^{++}$  is converted into  $\text{Ni}(\text{NH}_3)_4^{++}$ .

6. Give the formula for a chemical substance which will form a precipitate:

a. With  $\text{CrCl}_3$  solution but not with  $\text{Na}_2\text{CrO}_4$ .

b. With  $\text{MnCl}_2$  solution but not with  $\text{KMnO}_4$ .

c. With  $\text{FeCl}_3$  solution but not with  $\text{AlCl}_3$ .

d. With  $\text{Na}_2\text{CrO}_4$  solution but not with  $\text{Zn}(\text{NO}_3)_2$ .

e. With  $\text{NiCl}_2$  solution but not with  $\text{CrCl}_3$ .

f. With  $\text{MnCl}_2$  solution but not with  $\text{AlCl}_3$ .

g. With  $\text{FeCl}_3$  solution but not with  $\text{CoCl}_2$ .

h. With  $\text{CoCl}_2$  solution but not with  $\text{ZnCl}_2$ .

i. With  $\text{AlCl}_3$  solution but not with  $\text{ZnCl}_2$ .

j. With  $\text{Na}_2\text{CrO}_4$  solution but not with  $\text{FeCl}_3$ .

k. With  $\text{AlCl}_3$  solution but not with  $\text{CaCl}_2$ .

l. With  $\text{NiCl}_2$  solution but not with  $\text{BaCl}_2$ .

7. Give the formula for a reagent which will:

a. Dissolve  $\text{MnS}$  but not  $\text{NiS}$ .



- b. Dissolve  $\text{ZnS}$  but not  $\text{CuS}$ .
- c. Dissolve  $\text{Al}(\text{OH})_3$  but not  $\text{Fe}(\text{OH})_3$ .
- d. Dissolve  $\text{Ni}(\text{OH})_2$  but not  $\text{Fe}(\text{OH})_3$ .
- e. Dissolve  $\text{Cr}(\text{OH})_3$  but not  $\text{Bi}_2\text{S}_3$ .
- f. Dissolve  $\text{Zn}(\text{OH})_2$  but not  $\text{Ni}(\text{OH})_2$ .
- g. Dissolve  $\text{Na}_2\text{CrO}_4$  but not  $\text{Al}(\text{OH})_3$ .

8. Give the formula for a solid substance in the aluminum-nickel group which will:

- a. Dissolve in concentrated  $\text{HCl}$  but will not dissolve in concentrated  $\text{HNO}_3$ .
- b. Dissolve in  $\text{NaOH}$  but not in  $\text{NH}_4\text{OH}$ .
- c. Dissolve in  $\text{NH}_4\text{OH}$  but not in  $\text{NaOH}$ .
- d. Dissolve in  $\text{HCl}$  but not in water.
- e. Dissolve in  $\text{HCl}$  and also in  $\text{NaOH}$ .
- f. Dissolve in  $\text{HCl} + \text{HNO}_3$  but not in  $\text{HCl}$ .

9. On the addition of  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH}$  to a solution known to contain only cations of the aluminum-nickel group, a white flocculent precipitate forms. On further addition of  $\text{H}_2\text{S}$ , a black precipitate forms. The combined precipitate does not dissolve completely in  $\text{HCl}$  but dissolves completely in  $\text{HCl} + \text{HNO}_3$ . The resulting solution is green. When this solution is treated with excess  $\text{NaOH}$ , then with  $\text{Na}_2\text{O}_2$ , and filtered, the filtrate is colorless and the precipitate on the filter is light green. What conclusions can be drawn?

10. On addition of  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH}$  to a solution known to contain only cations of the aluminum-nickel group, a dark-red precipitate forms. On further addition of  $\text{H}_2\text{S}$ , a black precipitate forms. The combined precipitate dissolves readily and completely in  $\text{HCl}$ . The resulting green solution, having first been boiled with a few drops of concentrated  $\text{HNO}_3$ , gives a reddish-brown precipitate and a pale-green solution when treated with excess  $\text{NaOH}$ . On being treated with  $\text{Na}_2\text{O}_2$  the solution turns yellow, the precipitate undergoing no change in color. What conclusions can be drawn?

11. A solid material which was known to contain only cations of the aluminum-nickel group dissolved in  $\text{HCl}$  to give a green solution. The addition of  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH}$  gave a white precipitate, and the further addition of  $\text{H}_2\text{S}$  gave a black precipitate. This precipitate was dissolved in  $\text{HCl} + \text{HNO}_3$ . When the solution thus formed was treated with  $\text{NaOH}$  followed by  $\text{Na}_2\text{O}_2$ , a colorless solution and a reddish-brown precipitate were formed. This precipitate was found to be soluble in either  $\text{HCl}$  or  $\text{HNO}_3$ . What conclusions can be drawn?

12. A colorless solution known to contain only cations of the aluminum-nickel group was divided into three parts which were treated, respectively, as follows:

- a. To one part  $\text{NaOH}$  was added, slowly and with constant stirring. A light-colored precipitate formed, part of which redissolved in an excess of  $\text{NaOH}$ . The solution was centrifuged and decanted. The precipitate was observed to darken on standing exposed to the air.

b. The second part gave no precipitate on being treated with  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH}$ .

c. The third part gave a light-colored precipitate when treated with  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{OH}$ , and  $\text{H}_2\text{S}$ .

What conclusions can be drawn?

13. Using as few operations as possible, how test for the following?

a.  $\text{Zn}^{++}$  in a solution known to contain  $\text{Ni}^{++}$ .

b.  $\text{Mn}^{++}$  in a solution known to contain  $\text{Co}^{++}$  and  $\text{Cl}^-$ .

c.  $\text{Al}^{+++}$  in a solution known to contain  $\text{Cr}^{+++}$ .

d.  $\text{Fe}^{++}$  in a solution known to contain  $\text{Fe}^{+++}$ .

e.  $\text{Ni}^{++}$  in a solution known to contain  $\text{Fe}^{++}$ .

14. How would you distinguish, by means of one reagent, between the following? (Tell what happens to each substance.)

a. *Solutions:*

$\text{Na}_3\text{AlO}_3$  and  $\text{Al}(\text{NO}_3)_3$

$\text{CrCl}_3$  and  $\text{NiCl}_2$

$\text{MnCl}_2$  and  $\text{ZnCl}_2$

$\text{AlCl}_3$  and  $\text{ZnCl}_2$

$\text{FeCl}_3$  and  $\text{FeCl}_2$

$\text{FeCl}_3$  and  $\text{Na}_2\text{CrO}_4$

$\text{Zn}(\text{NH}_3)_4\text{Cl}_2$  and  $\text{ZnCl}_2$

$\text{ZnCl}_2$  and  $\text{BaCl}_2$

b. *Solids:*

$\text{ZnS}$  and  $\text{CoS}$

$\text{Ni}(\text{OH})_2$  and  $\text{Cr}(\text{OH})_3$

$\text{MnS}$  and  $\text{NiS}$

$\text{Na}_2\text{S}$  and  $\text{ZnS}$

$\text{Al}(\text{OH})_3$  and  $\text{Mn}(\text{OH})_2$

$\text{MnO}_2$  and  $\text{Fe}(\text{OH})_3$

$\text{Zn}(\text{OH})_2$  and  $\text{Al}(\text{OH})_3$

$\text{CuS}$  and  $\text{FeS}$

## **Aluminum-nickel group report**

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## CHAPTER 6

### The Barium-Magnesium Group

AFTER THE REMOVAL of the preceding groups, the ions of barium, calcium, magnesium, potassium, sodium, and ammonium remain in the solution being analyzed. Barium and calcium are members of the barium group. The remaining four will be called the magnesium group.

The separation of barium and calcium ions from the cations of the magnesium group depends on the fact that in an alkaline solution containing excess  $\text{NH}_4^+$  ions, calcium and barium are precipitated as  $\text{CaCO}_3$  and  $\text{BaCO}_3$  by  $(\text{NH}_4)_2\text{CO}_3$ , whereas magnesium, sodium, and potassium ions remain in solution.

#### Procedure 22: Precipitation of calcium and barium

If the solution to be analyzed is a barium-magnesium group "known" or "unknown," follow Method (A), below. If the decantate from Procedure 15 is being analyzed, follow (B).

(A) Place 6 drops of the solution to be analyzed in a test tube and add 10 drops of cold water (see Note 1). Then add 4 drops of 2N  $\text{NH}_4\text{Cl}$ , mix thoroughly, make alkaline with 15N  $\text{NH}_4\text{OH}$ , and add 4 drops of 4N  $(\text{NH}_4)_2\text{CO}_3$ . When precipitation is complete, centrifuge and decant, saving the decantate for Procedure 25. Wash the precipitate ( **$\text{CaCO}_3$ ,  $\text{BaCO}_3$** ) three times with cold water and analyze according to Procedure 23.

(B) Place the decantate from Procedure 15 in a casserole, evaporate to a volume of 7–8 drops, transfer to a test tube, and centrifuge. Decant into a casserole, discarding any precipitate. Add 2 drops of 6N  $\text{HCl}$ ; then evaporate the solution to dryness and bake until all ammonium salts are driven off. Cool. Then add 15 drops of hot water and stir for 1 minute.

Transfer the solution to a test tube; if the solution is clear, proceed as directed in the second sentence of (A). If the solution is not clear, then centrifuge, decant the clear supernatant liquid into a test tube, and proceed with it as directed in the second sentence of (A).

### NOTES

1. If the barium-magnesium group "unknown" is issued in the form of a finely divided solid, proceed as follows: Place in a test tube as much of the solid as can be carried on  $\frac{1}{4}$  in. of the tip of the spatula. Add 3-4 drops of 6N HCl, warm gently, and then add 10-12 drops of water. Mix thoroughly and heat carefully until a clear solution is obtained. Proceed with the analysis of the solution as directed in the second sentence of Procedure 22(A).

If the solid unknown is not finely divided when received, the entire sample should first be pulverized in a clean mortar.

2. Concentrating the solution before the precipitation of the barium group precipitates out, as sulfides or hydroxides, any cations of preceding groups which might be present in the decantate from the aluminum-nickel group.

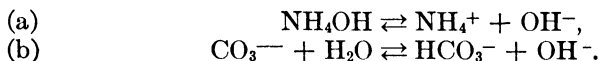
3. The decantate from the aluminum-nickel group contains a large excess of ammonium salts. Because  $\text{CaCO}_3$  and  $\text{BaCO}_3$  are appreciably soluble in the presence of large amounts of these salts, the latter are removed by sublimation.

4. Since  $\text{CaCO}_3$  and  $\text{BaCO}_3$  are somewhat soluble in water, they must be precipitated from relatively concentrated solutions. Dissolving the residue left after baking, in 15 drops of water, gives a sufficiently concentrated solution.

5. If no residue remains in the evaporating dish after the ammonium salts are sublimed, then barium, calcium, magnesium, sodium, and potassium are absent.

6.  $\text{NH}_4\text{Cl}$  is added to prevent the precipitation of magnesium as  $\text{Mg}(\text{OH})_2$  or  $\text{MgCO}_3$ . The role of  $\text{NH}_4\text{Cl}$  in preventing the precipitation of  $\text{Mg}(\text{OH})_2$  is discussed in Note 4 of Procedure 15. The prevention of the precipitation of  $\text{MgCO}_3$  is probably more involved. One possible interpretation is the following:  $\text{MgCO}_3$  will not precipitate if the concentration of  $\text{CO}_3^{2-}$  ions is kept sufficiently low. A high concentration of  $\text{NH}_4^+$  ions decreases the ionization of  $\text{NH}_4\text{OH}$ , thereby producing a lowered concentration of  $\text{OH}^-$  ions in Equation (a), below. Lowering the  $\text{OH}^-$  concentration causes the equilibrium point in the reaction of  $\text{CO}_3^{2-}$  ions (from  $(\text{NH}_4)_2\text{CO}_3$ ) with water to be

shifted to the right. Shifting the equilibrium point of Equation (b) to the right reduces the concentration of  $\text{CO}_3^{--}$  to the point where  $\text{MgCO}_3$  does not precipitate.



## SEPARATION OF BARIUM FROM CALCIUM

Calcium chromate is soluble in dilute acetic acid. Barium chromate is insoluble. Upon these facts is based the separation of barium ions from calcium ions.

### Procedure 23. Separation and detection of barium

Dissolve the precipitate from Procedure 22 in 2–3 drops of 1.5N HCl. Make just alkaline with 15N  $\text{NH}_4\text{OH}$  (see Note 1); then make just acid with 5N  $\text{HC}_2\text{H}_3\text{O}_2$  and then add an excess of 1 drop of 5N  $\text{HC}_2\text{H}_3\text{O}_2$  and 4 drops of cold water and mix thoroughly. Add 1 drop of N  $\text{K}_2\text{CrO}_4$ . If no yellow precipitate forms, barium is absent; in that case analyze the solution for calcium according to Procedure 24. If a yellow precipitate ( $\text{BaCrO}_4$ ) forms, barium is present; in that case add more  $\text{K}_2\text{CrO}_4$  until precipitation is complete. Centrifuge and decant, saving the decantate for Procedure 24. Wash the precipitate three times with hot water, dissolve it in 2 drops of 6N HCl, and make a flame test as directed in Note 2. A green coloration to the flame further proves the presence of barium.

### NOTES

1. A white precipitate,  $\text{Ba}(\text{OH})_2$  and  $\text{Ca}(\text{OH})_2$ , may form when  $\text{NH}_4\text{OH}$  is added. This precipitate will redissolve in  $\text{HC}_2\text{H}_3\text{O}_2$ .

2. Directions for making a flame test: Seal a 2-in. piece of platinum wire into one end of a 5-in. piece of glass tubing. This platinum wire will serve for all subsequent flame tests. Clean the platinum wire by alternately heating it to redness and thrusting it into concentrated HCl contained in a test tube until it gives no coloration to the non-luminous flame of the Bunsen burner.

Dip the clean platinum wire into the solution or precipitate to be tested; then hold it in the nonluminous flame and note any coloration.

The following ions give characteristic flame colorations: barium, green; borate, pale green; calcium, orange red; copper, green; potassium, violet through blue glass; sodium, yellow.

3. Since the chlorides of metals are in general more readily volatilized than other salts, chlorides are used in making the flame test.

4. The concentration of the acid present when barium is precipitated as  $\text{BaCrO}_4$  is very important. If the acid concentration is too high,  $\text{BaCrO}_4$  will not precipitate. If the concentration is too low,  $\text{CaCrO}_4$  will precipitate.

5. Since  $\text{CaCrO}_4$  may precipitate because of faulty acid concentration, it is desirable to verify barium by means of the flame test. The brilliant green of barium is readily distinguished from the orange-red calcium flame.

#### Procedure 24: Detection of calcium

Make the decantate from Procedure 23 (or, if barium is absent, the solution from Procedure 23) just alkaline with 15N  $\text{NH}_4\text{OH}$ ; then add 4–5 drops of 0.5N ammonium oxalate  $[(\text{NH}_4)_2\text{C}_2\text{O}_4]$ . A white precipitate ( $\text{CaC}_2\text{O}_4$ ) proves the presence of calcium. Centrifuge and decant, discarding the decantate. Wash the precipitate three times with hot water, dissolve it in 6N  $\text{HCl}$ , and run a flame test as directed in Note 2 of Procedure 23. An orange-red flame further proves the presence of calcium.

#### NOTES

1. Barium, if not completely removed in Procedure 23, would precipitate as white crystalline  $\text{BaC}_2\text{O}_4$ . Consequently, it is desirable to confirm calcium by the flame test.

2. Strontium, if included among the cations, would be present in the decantate from Procedure 23. The separation of strontium from calcium and the subsequent identification of strontium and calcium is presented in the reference texts listed at the end of Chapter 2. Strontium falls in periodic Group IIa, between calcium and barium. The chromates and sulfates of strontium are a little less soluble than those of calcium and a little more soluble than those of barium. The carbonates of all three metals are almost equally insoluble. The oxalates of strontium and barium are equally insoluble, but calcium oxalate is somewhat more insoluble than the other two. By taking

advantage of the solubility differences of the chromates, sulfates, and oxalates noted above, a fairly satisfactory separation of barium, strontium, and calcium can, with good technique, be accomplished. Since strontium is not a common metal and since the technique required for its separation is exacting, it has been omitted from the present scheme of analysis.

### Procedure 25: Separation and detection of magnesium

Treat the decantate from Procedure 22 with 2 drops of 2N  $(\text{NH}_4)_2\text{SO}_4$  and 2 drops of 0.5N ammonium oxalate, heat to boiling, cool, centrifuge, and decant, discarding any precipitate. Save one half of the decantate for the detection of sodium and potassium, Procedure 26; treat the other half with 2 drops of 2N  $\text{NH}_4\text{Cl}$ , 1 drop of 15N  $\text{NH}_4\text{OH}$ , and 3–4 drops of  $\text{Na}_2\text{HPO}_4$  solution. A white precipitate ( $\text{MgNH}_4\text{PO}_4$ ) shows the presence of magnesium (see Note 1). Centrifuge and decant, discarding the decantate. Wash the precipitate three times with hot water, dissolve in 2–3 drops of 1.5N  $\text{HCl}$ , and then add 1 drop of “magnesium reagent.” Then add 8N  $\text{NaOH}$ , with constant mixing, until the solution is distinctly alkaline. A blue “lake” (flocculent precipitate) proves the presence of magnesium.

### NOTES

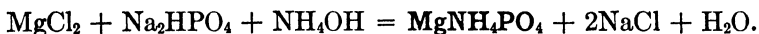
1. The precipitate of  $\text{MgNH}_4\text{PO}_4$  sometimes forms very slowly. If a precipitate does not form at once, heat to boiling, cool, and allow to stand for 1 minute. If no precipitate forms, magnesium is absent.

2. Since  $\text{CaCO}_3$  and  $\text{BaCO}_3$  are slightly soluble in alkaline solution, small amounts of calcium and barium may be present in the alkaline filtrate from Procedure 22. All calcium and barium must be removed before the confirmatory test for magnesium is made; otherwise they will precipitate as  $\text{Ba}_3(\text{PO}_4)_2$  and  $\text{Ca}_3(\text{PO}_4)_2$ . Since  $\text{BaSO}_4$  and  $\text{CaC}_2\text{O}_4$  are highly insoluble, barium and calcium ions will be removed if the solution is treated with  $(\text{NH}_4)_2\text{SO}_4$  and  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ .

3. Since the oxalates of most metals are quite insoluble, the addition of  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  and  $(\text{NH}_4)_2\text{SO}_4$  will not only remove barium and calcium ions but will also precipitate any other metallic ions that may have failed to precipitate completely in preceding groups. The re-

moval of these metallic ions is imperative, since they, like  $\text{Ba}^{++}$  and  $\text{Ca}^{++}$ , form insoluble phosphates which might be mistaken for  $\text{MgNH}_4\text{PO}_4$ . Magnesium oxalate is quite soluble and does not precipitate.

4. The white precipitate of magnesium ammonium phosphate is formed as follows:



Since  $\text{MgNH}_4\text{PO}_4$  is slightly soluble in warm water, the solution should be cooled.

5. Since phosphates of other metals besides magnesium may precipitate at this point, it is necessary to show that the precipitate is a magnesium compound. The special magnesium reagent is a solution of the complex organic dye *ortho-para*-dihydroxy azo-paranitrobenzene. It forms a blue precipitate or "lake" with very small amounts of magnesium ion. (A "lake" is formed when a dye is adsorbed by a precipitate.) Nickel and cobalt ions, if present, form similar blue lakes. Excess of ammonium ion reduces the sensitivity of the test by interfering with the formation of the lake.

## DETECTION OF SODIUM AND POTASSIUM

Since sodium and potassium form very few insoluble compounds, their separation by precipitation reactions is comparatively difficult. For this reason they are detected in the presence of each other. They can also be detected by means of their characteristic flame tests.

### Procedure 26: Detection of sodium and potassium

Evaporate the remaining half of the decantate from Procedure 25 to dryness and bake in the casserole until all  $\text{NH}_4\text{Cl}$  has sublimed off. Cool, treat with 1 drop of 6N HCl, and make a flame test. A fluffy yellow flame proves the presence of sodium. A reddish-violet coloration of short duration, when viewed through blue glass, proves the presence of potassium.

Add 5–6 drops of water to the solution in the casserole and mix thoroughly. Place 3 drops of this solution in a test tube, add 6 drops of zinc uranyl acetate solution, and mix thor-

oughly. A yellow crystalline precipitate,  $\text{NaZn}(\text{UO}_2)_3(\text{C}_2\text{H}_3\text{O}_2)_9$ , proves the presence of sodium.

Evaporate the solution remaining in the casserole to dryness, cool, add 4–5 drops of water, mix thoroughly, transfer to a test tube, and acidify with 5N  $\text{HC}_2\text{H}_3\text{O}_2$ . Add an equal volume of sodium cobaltinitrite solution, mix thoroughly, and warm gently. A yellow precipitate,  $\text{K}_2\text{NaCo}(\text{NO}_2)_6$ , proves the presence of potassium.

### NOTES

1. Ammonium salts sublime when heated and consequently make it difficult to detect the color of the sodium and potassium flames. Hence their removal by sublimation.

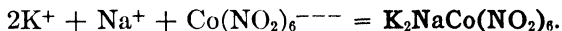
2. Sodium is commonly present as an impurity in many commercial salts. Also, it is introduced as impurity in the course of the metal analysis. For this reason a yellowish flame is almost invariably obtained. Sodium should not be reported unless the yellow flame is genuinely fluffy and strong. In case of doubt compare the intensity of the yellow flame with that given by a solution of common salt or sodium carbonate. When analyzing salts, a flame test should be run on a bit of the original solid moistened with HCl.

3. A green flame appears violet red when viewed through the blue glass. For this reason barium, copper, and borate ions must be absent when the flame test for potassium is made.

4. The glowing of the red-hot platinum wire must not be mistaken for a potassium test. Potassium, if present, will give a violet coloration to the flame the moment the wire is introduced.

5. The exact composition of zinc uranyl acetate has not been determined. The composition of the yellow crystalline precipitate has, however, been determined.

6. The yellow precipitate, potassium sodium cobaltinitrite is formed as follows:



### DETECTION OF AMMONIUM SALTS

When an ammonium salt is heated with a strong base, ammonia gas is evolved. This fact is the basis for the detection of ammonium. Since  $\text{NH}_4\text{Cl}$ , as well as other ammonium salts,

is added at various points in the cation analysis, the test for ammonium must be made on a sample of the original material.

### Procedure 27: Detection of ammonium

Place 5 drops of 8N NaOH solution in a test tube. Add 5 drops of the solution to be tested, or a pinch of the solid to be tested. Warm gently but do not boil. The evolution of  $\text{NH}_3$  gas, detected by its odor or by its reaction to a piece of moist red litmus held close to the end of the tube, proves the presence of ammonium compounds.

#### NOTE

Ammonia gas is evolved according to the following equation:



#### Questions

1. Using the scheme of analysis as a guide, write equations for all reactions that take place in the precipitation and analysis of the barium-magnesium group.
2. How account for the fact that there are no oxidation-reduction reactions in the barium-magnesium group?
3. Upon what fact or facts are the following based?
  - a. The separation of calcium and barium ions from magnesium, potassium, and sodium ions.
  - b. The separation of barium ions from calcium ions.
  - c. The confirmatory test for ammonium ions.
4. In the precipitation and analysis of the barium-magnesium group:
  - a. Why add  $\text{NH}_4\text{Cl}$  and  $\text{NH}_4\text{OH}$  before precipitating  $\text{CaCO}_3$  and  $\text{BaCO}_3$ ?
  - b. Why run a flame test on the original solid?
  - c. Why add a limited amount of dilute  $\text{H}_2\text{C}_2\text{O}_4$  before precipitating barium as  $\text{BaCrO}_4$ ?
  - d. Why convert barium and calcium to chlorides before making the flame tests?
  - e. Why sublime off  $\text{NH}_4$  salts before precipitating barium and calcium as carbonates?
  - f. Why precipitate barium and calcium as carbonates from a fairly concentrated solution?
  - g. Why add  $(\text{NH}_4)_2\text{SO}_4$  and  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  to the decantate from the



barium-group precipitation before making the confirmatory test for magnesium?

h. Why test for ammonium on a sample of the original material?

5. How would you distinguish between the following solids?

a.  $\text{NH}_4\text{Cl}$  and  $\text{NaCl}$ .

c.  $\text{BaCl}_2$  and  $\text{CaCl}_2$ .

b.  $\text{MgCO}_3$  and  $\text{K}_2\text{CO}_3$ .

d.  $(\text{NH}_4)_2\text{C}_2\text{O}_4$  and  $\text{NH}_4\text{Cl}$ .

6. A solution known to contain only cations of the barium-magnesium group gave a white precipitate when treated with  $\text{NH}_4\text{OH}$  and  $(\text{NH}_4)_2\text{CO}_3$  but gave no precipitate when treated with  $\text{NH}_4\text{Cl}$ ,  $\text{NH}_4\text{OH}$ , and  $(\text{NH}_4)_2\text{CO}_3$ . What conclusions can be drawn?

7. How would you test for:

a.  $\text{Mg}^{++}$  in a solution known to contain  $\text{Ca}^{++}$ ?

b.  $\text{K}^+$  in a solution known to contain  $\text{Ba}^{++}$ ?

c.  $\text{Ca}^{++}$  in a solution known to contain  $\text{Ba}^{++}$ ?

d.  $\text{Ba}^{++}$  in a solution known to contain  $\text{Mg}^{++}$ ?

8. Suppose you have discovered a new metal. What properties of the metal or of its compounds must you know in order to determine its proper place in the scheme of analysis for metallic ions?

## **Barium-magnesium group report**

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## Barium-magnesium group report

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## CHAPTER 7

### The Analysis of Alloys

WHEN TWO or more metals are melted together and the resulting liquid is cooled until completely solidified, the solid product is called an *alloy*. Alloys look like metals, behave very much like metals, and are used for much the same purposes. The physical properties of an alloy, such as melting point, hardness, malleability, ductility, tensile strength, coefficient of expansion, and conductivity, are different from the corresponding properties of the component metals. Furthermore, for an alloy prepared from a certain combination of metals, these properties will vary with the composition of the alloy and the particular treatment it receives. Metals such as iron, copper, aluminum, and magnesium are versatile materials for building machines, machine parts, utensils, tools, and structures of all kinds. Alloys are even more versatile. It is possible, by bringing together the proper metals in the proper proportions, to get alloys with almost any property desired. As a result, hundreds of alloys are in use, each with its own set of desirable properties. Some alloys, such as brass (copper and zinc), bronze (copper and tin), and monel metal (nickel, copper, and iron) are used in a wide variety of products, whereas others, such as invar (iron and nickel), have very specific uses.

Rare metals, such as molybdenum, tungsten, vanadium, and cerium, are often found in iron alloys, being intentionally introduced to give certain desirable properties to the steel. Stainless steels contain notable amounts of chromium.

*Amalgams* are alloys in which mercury is one of the metals used. Since most of the metals are soluble in mercury, a common method of preparing amalgams is that of simple solution of the metal in liquid mercury.

The table below lists a few of the more common alloys. The compositions given are in most instances only approximate; even an alloy as standard as sterling silver may show slight variations in the per cent of silver and copper.

COMPOSITION OF SOME IMPORTANT ALLOYS

<i>Name</i>	<i>Composition (percentage)</i>
Aluminum brass . . .	Cu 68-70, Zn 27-31, Al 1-3
Aluminum bronze . . .	Cu 90, Al 10
Babbitt metal . . .	Sn 70-90, Sb 7-24, Cu 2-22
Bell metal (bronze) . .	Cu 75-80, Sn 20-25
Britannia . . .	Sn 90-95, Sb 5-10, Cu 1-3
Brass . . . . .	Cu 65-75, Zn 25-35
Duralumin . . .	Al 95.5, Cu 3, Mn 1, Mg 0.5
German silver . . .	Cu 55, Ni 20, Zn 25
Invar . . . . .	Fe 64, Ni 36
Magnalium . . . . .	Al 90-94, Mg 6-10
Manganese bronze . . .	Cu 56, Zn 41, Sn 0.5, Fe 1, Mn 0.5, Al 1
Monel metal . . .	Ni 72, Cu 26.5, Fe 1.5
Nichrome . . .	Ni 60, Cr 40
Nickel coins . . .	Cu 75, Ni 25
Pewter . . . . .	Sn 85-90, Sb 10-13 (Pb) (Cu) (Bi)
Solder (medium) . . .	Pb 50, Sn 50
Sterling silver . . .	Ag 92.5, Cu 7.5
Type metal . . . . .	Pb 60-85, Sb 8-20, Sn 5-35
Wood's metal . . . . .	Bi 38, Pb 31, Sn 15, Cd 16

The analysis of an alloy involves two separate steps; first, a qualitative analysis to determine what metals are present, then a quantitative analysis to determine the exact percentage of each of the component parts. This chapter is concerned only with the qualitative analysis.

Nonmetals are frequently found in alloys, sometimes as impurities, sometimes added intentionally to give the alloy certain properties. Phosphorus in bronze, where it is present as a metallic phosphide, gives hardness to that alloy. Silicon in certain cast irons may be present to the extent of 15 per cent. Iron-silicon alloys are especially resistant to acid corrosion. The qualitative analysis of an alloy may therefore involve not only the detection of the metals but also of such nonmetals as silicon, carbon, phosphorus, and sulfur. The procedures outlined in this chapter, however, include only

the separation and identification of the metallic constituents of an alloy.

### Procedure 28: Dissolving an alloy

Place a quantity of the alloy about one-eighth to one-tenth the volume of a drop of water in a casserole (see Note 1). Add 3 drops of 16N  $\text{HNO}_3$  and 12 drops of 12N  $\text{HCl}$ , and boil gently under a hood. Replenish the acids in the ratio of 1 drop of 16N  $\text{HNO}_3$  to 4 drops of 12N  $\text{HCl}$  as fast as the liquid boils away, continuing the boiling until the alloy is completely dissolved (see Note 2). Then add excess 16N  $\text{HCl}$  and boil until no more  $\text{NO}_2$  or  $\text{Cl}_2$  is evolved; finally, evaporate to a volume of about 8 drops, add 5 drops of water, and allow to cool. If no precipitate is present in the solution in the casserole, silver is absent and lead is probably absent; then proceed with the analysis as directed in the second sentence of Part (A) of Procedure 5. If a white precipitate is present in the solution in the casserole, proceed as follows: transfer the contents of the casserole to a test tube, cool under the tap, centrifuge, and decant. Analyze the precipitate as directed in Procedure 2 and analyze the decantate as directed in Procedure 5(B).

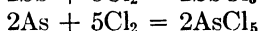
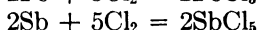
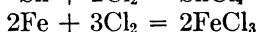
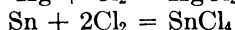
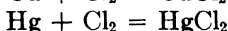
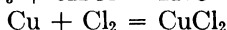
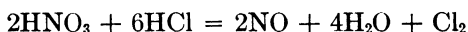
### NOTES

1. Commercial alloys are usually found in the form of castings, machined articles, instrument parts, rods, plates, bolts, wire, and so on. When an alloy is to be analyzed, a small amount is filed off or a hole is drilled in the specimen, or a sample is machined on a lathe or milling machine and the filings, drillings, borings, turnings, or millings thus obtained are subjected to analysis. The alloys to be analyzed in this course will usually be issued in the form of such filings, drillings, borings, turnings, and millings. Some of the alloys are authentic commercial specimens; some are synthetic products prepared solely for the purpose of giving the student experience in alloy analysis.

2. Dissolving an alloy is often a very slow process requiring long boiling and numerous acid replenishings. If the alloy appears to be partly or wholly insoluble, the instructor should be consulted.

3. The mixture of  $\text{HCl}$  and  $\text{HNO}_3$  used for dissolving the alloy is known as *aqua regia*. Its powerful solvent action is probably due to

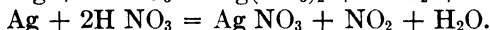
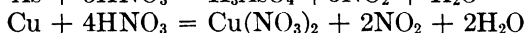
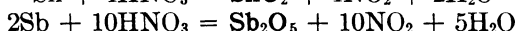
the liberation of chlorine; it will dissolve all metals, converting them to their chlorides (see Note 3, Procedure 7):



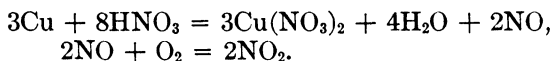
4. Silver chloride is insoluble and will, accordingly, be present in the casserole as a white curdy residue. Lead chloride is only sparingly soluble and, unless present in very small amounts, will be found in the casserole as a white crystalline precipitate.

5. Aqua regia, being a powerful oxidizing agent, will oxidize mercury to its high valence. Consequently, no  $\text{Hg}_2\text{Cl}_2$  will precipitate, even though mercury is present in the alloy. Tin, iron, and arsenic, like mercury, will be converted to their high-valenced chlorides.

6. Hot concentrated  $\text{HNO}_3$ , alone, will react with all of the metals that are considered in this course. Antimony and tin are converted to white, insoluble  $\text{Sb}_2\text{O}_5$  and  $\text{SnO}_2$ , respectively, whereas arsenic forms soluble arsenic acid,  $\text{H}_3\text{AsO}_4$ . The other metals are all converted to soluble nitrates:



Less concentrated  $\text{HNO}_3$  will yield colorless NO rather than brown  $\text{NO}_2$ . However, when NO comes in contact with air it is converted to brown  $\text{NO}_2$ :

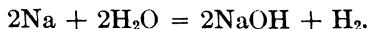


$\text{SnO}_2$  and  $\text{Sb}_2\text{O}_5$  will dissolve in  $\text{HCl}$  to form  $\text{SnCl}_4$  and  $\text{SbCl}_3$ . A scheme of alloy analysis using  $\text{HNO}_3$  alone as the initial solvent can be worked out; such a scheme is, however, not as satisfactory for all alloys as is the present one using aqua regia.

7. Sodium, potassium, calcium, and barium are seldom found in



commercial alloys. Alloys containing these metals react with water to evolve hydrogen:



Since ammonium exists only as a radical, there obviously is no such thing as a stable ammonium alloy.

8. The color of the solution obtained when an alloy is dissolved in aqua regia may give valuable clues as to the metals present. As has been noted already, the following metals form colored chlorides:  $\text{CuCl}_2$ , green;  $\text{FeCl}_3$ , yellowish brown;  $\text{CrCl}_3$ , green;  $\text{NiCl}_2$ , green;  $\text{CoCl}_2$ , reddish pink or blue;  $\text{MnCl}_2$ , faint pink.

9. It will be noted, in the equations given in Notes 3, 6, and 7, that the metals in an alloy react exactly as if they were separate pure metals. These reactions might lead to the conclusion that an alloy is simply a mixture of metals. Some alloys are, in fact, very intimate mixtures. In a great many alloys, however, the component metals exist as compounds. In general it may be stated that most alloys are very complex in structure.

### Questions

1. Show by means of outlines the complete analysis of alloys containing the following metals:

- Sn, Ag, Cu, Fe, Zn, Mg.
- Pb, Hg, Bi, Mn, Al.
- As, Sb, Cd, Ni, Cr.

2. Show, by appropriate equations, what happens when each of the following is dissolved in aqua regia: mercury, iron, copper, tin, arsenic, antimony, chromium, silver.

3. Show, by appropriate equations, what happens when each of the following is treated with hot concentrated  $\text{HNO}_3$ : arsenic, antimony, tin, mercury, lead, silver, iron, copper.

4. Using the simplest chemical method possible, how distinguish between the following metals?

- Tin and zinc.
- Nickel and silver.
- Iron and antimony.
- Arsenic and antimony.
- Lead and bismuth.
- Magnesium and zinc.
- Chromium and nickel.

5. Using the simplest method possible, how determine whether an alloy is brass (Cu-Zn) or bronze (Cu-Sn)?

6. An alloy showed the following behavior:

- a. It was attacked by  $\text{HNO}_3$  to give a colorless supernatant liquid and a finely divided white residue. This residue was soluble in  $\text{HCl}$ .
- b. It was attacked by aqua regia to give a colorless solution and a white, curdy residue.
- c. It was not acted upon by water.

What conclusions can be drawn?

7. An alloy was found to be completely dissolved (a) by cold moderately concentrated  $\text{HNO}_3$ , (b) by cold dilute  $\text{HCl}$ , and (c) by cold dilute  $\text{H}_2\text{SO}_4$ . In each case it gave a colorless solution with no precipitate. What conclusions can be drawn?

## **Alloy report**

## **Alloy report**

## **Alloy report**

## CHAPTER 8

### Preliminary Tests for Anions

*To the student:* Up to this point you have learned how to separate and identify the cations (metallic ions) and you have applied this information to the analysis of four group unknowns and an alloy. The next unknown that you will analyze will be a single salt or a mixture of salts. To analyze a salt, you must identify the anions (acid radicals) as well as the cations. Consequently, before you can proceed with the analysis of your first salt or salt mixture you must learn how to identify the anions. To aid you in learning how to identify the anions, you will perform Experiments 1, 2, 3, and 4 as described on pages 137, 140, 144, and 150.

When you have performed these experiments and have acquainted yourself with the discussion relating to these experiments you will be ready to proceed with the analysis of your first salt according to the directions given in Chapter 10.

The complete analysis of a salt or mixture of salts calls for identification of the anions (acid radicals) as well as the cations (metallic ions). The separation and identification of the cations has been presented in Chapters 3, 4, 5, 6, and 7. The identification of the anions will be presented in this chapter and in Chapter 9.

Only the following 13 anions will be considered: acetate,  $\text{C}_2\text{H}_3\text{O}_2^-$ ; nitrate,  $\text{NO}_3^-$ ; chloride,  $\text{Cl}^-$ ; bromide,  $\text{Br}^-$ ; iodide,  $\text{I}^-$ ; sulfide,  $\text{S}^{2-}$ ; sulfate,  $\text{SO}_4^{2-}$ ; sulfite,  $\text{SO}_3^{2-}$ ; carbonate,  $\text{CO}_3^{2-}$ ; chromate,  $\text{CrO}_4^{2-}$ ; phosphate,  $\text{PO}_4^{3-}$ ; arsenate,  $\text{AsO}_4^{3-}$ ; borate,  $\text{BO}_2^-$  or  $\text{BO}_3^{3-}$ . This list represents less than one-third of the anions that one might encounter in a course in general chemistry; it does, however, include the more common ones, and the methods and principles used in the identification of these 13 will serve to illustrate the methods and principles used for the identification of all others.

The detection of the cations was accomplished by a very logical sequence of procedures involving, first, separation and, second, identification. The detection of the anions does

not proceed in quite the same way; that is, it does not consist of a methodical sequence of separations and identifications. Instead it proceeds as follows: First, the material being analyzed is submitted to a series of so-called "preliminary tests." As a result of these preliminary tests, certain of the anions may be shown definitely to be absent. That is, the preliminary tests may eliminate certain of the anions, thereby paring down the number of possibilities from thirteen to some lesser number. Next, specific tests are carried out, on small samples of the material, for those anions not definitely eliminated in the preliminary tests. Although this sequence of preliminary tests and specific tests is not quite as well ordered as the procedures for cation analysis, it proceeds very logically and makes possible a rapid and systematic identification of the anions.

The preliminary tests for anions will be presented in this chapter. The specific tests for the anions will be presented in Chapter 9. The complete analysis of salts and salt mixtures, for anions and cations, will be discussed in Chapter 10.

The three preliminary tests that are used for the elimination of anions are:

1. Treatment of the solid unknown material with concentrated  $\text{H}_2\text{SO}_4$ .
2. Treatment of a solution of the anions with silver nitrate. This is commonly referred to as the group test for the hydrochloric acid group.
3. Treatment of a solution of the anions with barium chloride. This is commonly referred to as the group test for the sulfuric acid group.

### TREATMENT OF THE SOLID WITH CONCENTRATED $\text{H}_2\text{SO}_4$

When dry salts of each of the 13 acids are treated with concentrated sulfuric acid, certain very characteristic reactions are noted. These reactions, together with the changes that are observed, are summarized in the following table.

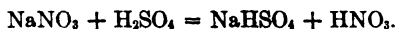
A. REACTIONS OF SALTS WITH COLD CONCENTRATED  $\text{H}_2\text{SO}_4$ 

<i>Anion</i>	<i>Observation</i>	<i>Equations</i>
$\text{C}_2\text{H}_3\text{O}_2^-$	No evidence of reaction	
$\text{SO}_4^{--}$	No evidence of reaction	
$\text{PO}_4^{---}$	No evidence of reaction	
$\text{BO}_3^{---}$	No evidence of reaction	
$\text{AsO}_4^{---}$	No evidence of reaction	
$\text{NO}_3^-$	No evidence of reaction	
$\text{Cl}^-$	Effervescence. The gas evolved is colorless, has sharp odor, fumes in moist air, turns blue litmus red	$\text{NaCl} + \text{H}_2\text{SO}_4 = \text{NaHSO}_4 + \text{HCl}$
$\text{Br}^-$	Effervescence. The gas evolved is brown, has characteristic sharp odor, fumes in moist air, turns blue litmus red	$\text{NaBr} + \text{H}_2\text{SO}_4 = \text{NaHSO}_4 + \text{HBr}$ $\text{H}_2\text{SO}_4 + 2\text{HBr} = 2\text{H}_2\text{O} + \text{SO}_2 + \text{Br}_2$
$\text{I}^-$	Effervescence. Solid turns dark brown instantly, slight evolution of gas which fumes in moist air, odor of $\text{H}_2\text{S}$ , violet fumes of iodine	$\text{NaI} + \text{H}_2\text{SO}_4 = \text{NaHSO}_4 + \text{HI}$ $\text{H}_2\text{SO}_4 + 8\text{HI} = \text{H}_2\text{S} + 4\text{H}_2\text{O} + 4\text{I}_2$ $\text{H}_2\text{SO}_4 + 2\text{HI} = 2\text{H}_2\text{O} + \text{SO}_2 + \text{I}_2$
$\text{S}^{--}$	Effervescence. Odor of $\text{H}_2\text{S}$ gas, free sulfur deposited	$\text{ZnS} + \text{H}_2\text{SO}_4 = \text{ZnSO}_4 + \text{H}_2\text{S}$ $\text{H}_2\text{SO}_4 + \text{H}_2\text{S} = 2\text{H}_2\text{O} + \text{SO}_2 + \text{S}$
$\text{CO}_3^{--}$	Effervescence. Colorless, odorless gas	$\text{Na}_2\text{CO}_3 + \text{H}_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} + \text{CO}_2$
$\text{SO}_3^{--}$	Effervescence. Colorless gas with a sharp choking odor	$\text{Na}_2\text{SO}_3 + \text{H}_2\text{SO}_4 = \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} + \text{SO}_2$
$\text{CrO}_4^{--}$	Color changes from yellow to orange red	$2\text{K}_2\text{CrO}_4 + \text{H}_2\text{SO}_4 = \text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{O} + \text{K}_2\text{SO}_4$

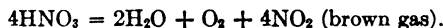
B. REACTIONS OF SALTS WITH HOT CONCENTRATED  $\text{H}_2\text{SO}_4$ 

1. Sulfates, phosphates, borates, and arsenates show no reaction on being heated with  $\text{H}_2\text{SO}_4$ .

2. Nitrates give brown fumes of  $\text{NO}_2$  when heated with  $\text{H}_2\text{SO}_4$ :



When  $\text{HNO}_3$  is heated, a part of it decomposes as follows:



3. Acetates yield acetic acid when warmed with  $\text{H}_2\text{SO}_4$ . The acetic acid has the characteristic odor of vinegar.



4. Chlorides, bromides, iodides, sulfides, carbonates, sulfites, and chromates show no additional reactions on being heated.



**Experiment 1: Treatment of a solid salt of each anion with  $\text{H}_2\text{SO}_4$ .** On the reagent shelf will be found solid salts of each of the 13 acids for which tests are to be made. Treat a pinch of the solid salt of each of them with concentrated sulfuric acid as directed in Procedure 29. Note exactly what happens in each case, record your observations in the table below, and compare these observations with those given in the preceding table. Write the equations for the reactions that take place. Have the results of this experiment approved by your instructor before proceeding with the next experiment.

Salt	Observations	Equations
$\text{NaNO}_3$		
$\text{NaCl}$		
$\text{NaBr}$		
$\text{NaI}$		
$\text{ZnS}$		
$\text{Na}_2\text{CO}_3$		
$\text{Na}_2\text{SO}_3$		
$\text{Na}_2\text{CrO}_4$		
$\text{Na}_2\text{SO}_4$		
$\text{NaBO}_2$		
$\text{Na}_3\text{PO}_4$		
$\text{Na}_3\text{AsO}_4$		
$\text{NaC}_2\text{H}_3\text{O}_2$		

**Procedure 29: Treatment of the solid material with concentrated  $\text{H}_2\text{SO}_4$** 

Place in a small test tube as much of the solid as can be carried on  $\frac{1}{4}$  in. of the tip of the spatula. Add one or two drops of 36N  $\text{H}_2\text{SO}_4$ . Notice everything that happens, particularly the color and odor of escaping gases. (Do not place your nose over the mouth of the test tube but fan any gas toward your nose held a few inches away.) Then heat, but not so strongly that the  $\text{H}_2\text{SO}_4$  is boiled, and note what happens. Finally heat the sides of the test tube over its entire length and note whether or not brown fumes ( $\text{NO}_2$ ) are formed (see Note 3).

List all anions whose presence or absence is indicated by this test.

**NOTES**

1. The reactions observed when single salts are treated with concentrated  $\text{H}_2\text{SO}_4$  are usually very definite and easy to interpret. However, when a mixture of salts is treated with  $\text{H}_2\text{SO}_4$ , the observations may be both indefinite and misleading because the reactions of one salt may completely mask other reactions. Thus, if iodides are present their very violent reactions with  $\text{H}_2\text{SO}_4$  may cover up the presence of all other anions. Likewise, bromides may cover up everything except iodides and chromates.

2. If only small quantities of certain salts, such as chlorides, nitrates, acetates, and sulfides, are present, treatment with sulfuric acid may show no definite reaction. For this reason, the eliminations of anions made on the basis of this test should not be considered as absolutely final.

3. Nitric acid decomposes only at relatively high temperatures. Furthermore, it is most readily decomposed by heating its vapors. Consequently, the test tube is heated over its entire length. If only small quantities of  $\text{HNO}_3$  are present, it may be necessary to look down into the test tube in order to observe the brown fumes. When looking into the test tube do not hold it closer than 18 in. from the eye.

4. When concentrated sulfuric acid comes in contact with moisture, a strongly exothermic reaction takes place. This may result in the evolution of steam accompanied by sputtering if the sample is moist. Care should be taken not to mistake this effect for effervescence.

### TREATMENT OF A SOLUTION OF THE ANIONS WITH $\text{AgNO}_3$

The silver salts of all thirteen anions except nitrate, acetate, and sulfate are insoluble in water. These insoluble silver salts have the following characteristic colors:  $\text{AgCl}$ , white;  $\text{AgBr}$ , cream;  $\text{AgI}$ , pale yellow;  $\text{Ag}_2\text{S}$ , dark brown;  $\text{Ag}_3\text{AsO}_4$ , chocolate brown;  $\text{Ag}_3\text{PO}_4$ , yellow;  $\text{Ag}_2\text{CrO}_4$ , red;  $\text{Ag}_2\text{CO}_3$ ,  $\text{Ag}_2\text{SO}_3$ , and  $\text{AgBO}_2$ , white.  $\text{AgCl}$ ,  $\text{AgBr}$ ,  $\text{AgI}$ , and  $\text{Ag}_2\text{S}$  are insoluble in dilute  $\text{HNO}_3$ ;  $\text{Ag}_2\text{CrO}_4$  is slightly soluble in dilute  $\text{HNO}_3$ ;  $\text{Ag}_3\text{AsO}_4$ ,  $\text{Ag}_3\text{PO}_4$ ,  $\text{Ag}_2\text{CO}_3$ ,  $\text{Ag}_2\text{SO}_3$ , and  $\text{AgBO}_2$  are soluble in dilute  $\text{HNO}_3$ . Accordingly, if silver ions, in the form of a solution of silver nitrate, are added to water solutions containing the 13 anions, the 10 insoluble silver salts listed above will precipitate. If each precipitate is, in turn, treated with dilute  $\text{HNO}_3$ , all but  $\text{AgCl}$ ,  $\text{AgBr}$ ,  $\text{AgI}$ ,  $\text{Ag}_2\text{S}$ , and  $\text{Ag}_2\text{CrO}_4$  will dissolve readily. If the solution containing the anions is acidified with dilute  $\text{HNO}_3$  before addition of  $\text{AgNO}_3$ , only  $\text{AgCl}$ ,  $\text{AgBr}$ ,  $\text{AgI}$ ,  $\text{Ag}_2\text{S}$ , and  $\text{Ag}_2\text{CrO}_4$  will precipitate;  $\text{Ag}_2\text{CrO}_4$  will not precipitate if the concentration of chromate ions in the original solution is low. The acids  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI}$ , and  $\text{H}_2\text{S}$ , whose silver salts are insoluble in  $\text{HNO}_3$ , are known as the *hydrochloric acid group*.

**Experiment 2: Treatment of a solution of the anions with silver nitrate.**

(A) Place 3–4 drops of a solution of the sodium salt of each of the anions, respectively, in 13 test tubes. Add a drop or two of 0.25N  $\text{AgNO}_3$  to each. Note the colors of the precipitates formed. Centrifuge and decant, saving the precipitate for Part (B). In the following spaces write the ionic equations for the formation of the precipitates obtained with  $\text{AgNO}_3$ . *Underline the precipitates* and indicate their colors.

$\text{C}_2\text{H}_3\text{O}_2^-$	_____
$\text{NO}_3^-$	_____
$\text{Cl}^-$	_____
$\text{Br}^-$	_____
$\text{I}^-$	_____
$\text{S}^-$	_____
$\text{CO}_3^-$	_____
$\text{SO}_3^-$	_____
$\text{CrO}_4^-$	_____
$\text{BO}_2^-$	_____
$\text{PO}_4^-$	_____
$\text{AsO}_4^-$	_____
$\text{SO}_4^-$	_____

(B) Attempt to dissolve each of the precipitates obtained in (A) in 2–3 drops of 3N  $\text{HNO}_3$ . In the spaces below write equations for those cases in which the silver salts are *dissolved* by dilute  $\text{HNO}_3$ . Indicate gases evolved by an upward arrow.

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

\_\_\_\_\_

List the silver salts *not dissolved* by dilute  $\text{HNO}_3$ :

Taking into account the results obtained in 2(A) and 2(B), list the anions which will react with  $\text{AgNO}_3$  to form precipitates in dilute nitric acid solution. \_\_\_\_\_

What name is given to this group of anions? \_\_\_\_\_

Have the results of this experiment approved by your instructor before going on with the next experiment.

**Procedure 30: Treatment of the solution of the anions with  $\text{AgNO}_3$** 

If the salt or mixture of salts is completely soluble in water, follow (A). If the salt is not completely soluble in water, follow (C).

(A) *The salt or salt mixture is soluble in water* (see Note 1 for a scheme of analysis). Place 10 drops of the water solution in a test tube; then add 3–4 drops of 0.25N  $\text{AgNO}_3$ . If no precipitate forms,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{S}^{--}$ ,  $\text{AsO}_4^{--}$ ,  $\text{PO}_4^{--}$ ,  $\text{CrO}_4^{--}$ ,  $\text{CO}_3^{--}$ ,  $\text{SO}_3^{--}$ , and  $\text{BO}_2^-$  are shown to be absent. If a precipitate forms, any or all 13 anions may be present; if the precipitate is white,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{S}^{--}$ ,  $\text{AsO}_4^{--}$ ,  $\text{PO}_4^{--}$ , and  $\text{CrO}_4^{--}$  are absent but the others may be present; if the precipitate is black, all 13 anions may be present, since black will cover up all other colors. Note the exact color of the precipitate and try, by means of the list given above, to decide what it is.

Centrifuge and decant, discarding the decantate. Wash the precipitate in the test tube once with cold water; then treat it with a few drops of 3N  $\text{HNO}_3$ , and stir. If the precipitate dissolves completely,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ , and  $\text{S}^{--}$  are absent; if the precipitate is not completely dissolved, one or more of the five anions just enumerated is present. Note carefully the appearance of the residue and if possible try to decide what it is.

Centrifuge and decant into a test tube. Save the decantate for Part (B).

(B) Make the decantate from Part (A) just alkaline with 15N  $\text{NH}_4\text{OH}$ ; then make it just acid with 5N acetic acid and then add a few drops of 0.25N  $\text{AgNO}_3$ . The following precipitates may form if the required anions are present:  $\text{Ag}_2\text{CrO}_4$ , red;  $\text{Ag}_3\text{AsO}_4$ , chocolate brown;  $\text{Ag}_3\text{PO}_4$ , yellow;  $\text{AgBO}_2$ , white.

On the basis of the observations made in (A) and (B), what anions, if any, are definitely shown to be absent? What anions are shown to be present?

(C) *The salt or salt mixture is not soluble in water*. A solution, for use in this Procedure and also in Procedure 31, must first be prepared as directed in Procedure 46(C), page 166.



### TREATMENT OF A SOLUTION OF THE ANIONS WITH $\text{BaCl}_2$

$\text{BaCl}_2$ ,  $\text{BaBr}_2$ ,  $\text{BaI}_2$ ,  $\text{BaS}$ ,  $\text{Ba}(\text{C}_2\text{H}_3\text{O}_2)_2$ , and  $\text{Ba}(\text{NO}_3)_2$  are soluble in water and in alkaline solution.  $\text{BaSO}_4$ ,  $\text{BaSO}_3$ ,  $\text{BaCO}_3$ ,  $\text{BaCrO}_4$ ,  $\text{Ba}_3(\text{AsO}_4)_2$ ,  $\text{Ba}_3(\text{PO}_4)_2$ , and  $\text{Ba}(\text{BO}_2)_2$  are insoluble in water and in alkaline solution.  $\text{BaSO}_4$  is insoluble in strong acids, such as dilute  $\text{HNO}_3$  or dilute  $\text{HCl}$ ; the other water-insoluble barium salts are soluble in dilute  $\text{HNO}_3$  or dilute  $\text{HCl}$ . These facts are the basis for the use of barium chloride as a reagent for the elimination of anions.

The anions whose barium salts are insoluble in water ( $\text{SO}_4^{--}$ ,  $\text{SO}_3^{--}$ ,  $\text{CO}_3^{--}$ ,  $\text{CrO}_4^{--}$ ,  $\text{AsO}_4^{--}$ ,  $\text{PO}_4^{--}$ , and  $\text{BO}_2^-$ ) are commonly referred to as the *sulfuric acid group*.  $\text{BaCrO}_4$  is yellow; the other barium salts are white.

**Experiment 3: Treatment of a solution of the anions with barium chloride.**

(A) Place 3–4 drops of a solution of the sodium salt of each of the anions, respectively, in 13 test tubes. Make each solution alkaline with a drop of 5N  $\text{NH}_4\text{OH}$  and then add a drop or two of N  $\text{BaCl}_2$  to each. Note the colors of all precipitates formed. Centrifuge, decant, and wash twice with cold water. Save each precipitate for Part (B).

In the following spaces write the ionic equations for the formation of the precipitates obtained with  $\text{BaCl}_2$  in alkaline ( $\text{NH}_4\text{OH}$ ) solution. *Underline the precipitates and indicate their colors.*

$\text{C}_2\text{H}_3\text{O}_2^-$  \_\_\_\_\_  
 $\text{NO}_3^-$  \_\_\_\_\_  
 $\text{Cl}^-$  \_\_\_\_\_  
 $\text{Br}^-$  \_\_\_\_\_  
 $\text{I}^-$  \_\_\_\_\_  
 $\text{S}^-$  \_\_\_\_\_  
 $\text{CO}_3^-$  \_\_\_\_\_  
 $\text{SO}_3^-$  \_\_\_\_\_  
 $\text{CrO}_4^-$  \_\_\_\_\_  
 $\text{BO}_2^-$  \_\_\_\_\_  
 $\text{PO}_4^-$  \_\_\_\_\_  
 $\text{AsO}_4^-$  \_\_\_\_\_  
 $\text{SO}_4^-$  \_\_\_\_\_

(B) Attempt to dissolve each of the precipitates from (A) in 4–5 drops of 1.5N  $\text{HCl}$ .

In the spaces below, write equations for those cases in which the barium salts are dissolved by dilute  $\text{HCl}$ . Note in which cases gases are evolved.

\_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_

List the barium salts that are not dissolved by dilute  $\text{HCl}$ . \_\_\_\_\_

List the anions which will react with  $\text{Ba}^{++}$  to form precipitates in alkaline solution. \_\_\_\_\_

\_\_\_\_\_ What name is given to this group of anions? \_\_\_\_\_

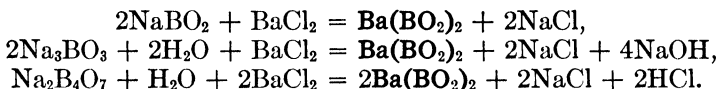
Have the results of this experiment approved by your instructor before proceeding with the next experiment.





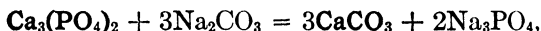
2. Since barium borate precipitates very slowly, the absence of a precipitate in the group test for the sulfuric acid group does not positively eliminate borates. A specific test for borates should always be made.

3. Although boron may be present as either the metaborate ( $\text{BO}_2^-$ ), the orthoborate ( $\text{BO}_3^-$ ), or the tetraborate ( $\text{B}_4\text{O}_7^-$ ), it is largely precipitated as the metaborate  $\text{Ba}(\text{BO}_2)_2$ :



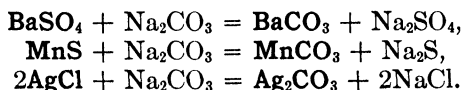
4. In preparing a solution for making the preliminary tests for anions, a water-insoluble unknown is boiled with  $\text{Na}_2\text{CO}_3$ . The object of this procedure is to precipitate all metals except sodium, potassium, and ammonium as carbonates. If they are not removed, they interfere with the group test for the  $\text{H}_2\text{SO}_4$  group. To illustrate the necessity of removing these metals by precipitation, suppose that the unknown contains  $\text{Ca}_3(\text{PO}_4)_2$ , and suppose it is dissolved in dilute  $\text{HCl}$ . In making the test for the sulfuric acid group, the acid solution must first be made alkaline with  $\text{NH}_4\text{OH}$ . As soon as this is done,  $\text{Ca}_3(\text{PO}_4)_2$  precipitates; there will then be no phosphate ions left in solution and the group test with  $\text{BaCl}_2$  will be negative.

If instead of being dissolved in dilute  $\text{HCl}$  the above unknown is boiled with  $\text{Na}_2\text{CO}_3$ , the  $\text{Ca}_3(\text{PO}_4)_2$  will react as follows:

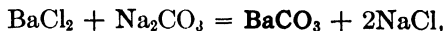


most of the  $\text{Ca}_3(\text{PO}_4)_2$  being converted into insoluble  $\text{CaCO}_3$ . On centrifuging and decanting, all the calcium will be found in the precipitate as  $\text{CaCO}_3$  and  $\text{Ca}_3(\text{PO}_4)_2$ , whereas, most of the phosphate will be present in the decantate as the phosphate ion. When the decantate is now made alkaline with  $\text{NH}_4\text{OH}$ , no precipitate will form, since all the calcium ions have been removed. On addition of  $\text{BaCl}_2$ , a white precipitate of  $\text{Ba}_3(\text{PO}_4)_2$  will form.

Insoluble salts of other metals will behave like  $\text{Ca}_3(\text{PO}_4)_2$ :



5. The solution prepared by boiling a water-insoluble salt with sodium carbonate also contains a large amount of the  $\text{Na}_2\text{CO}_3$  used in preparing this solution. This  $\text{Na}_2\text{CO}_3$  must be destroyed; otherwise it will react with the  $\text{BaCl}_2$  when the group test for the  $\text{H}_2\text{SO}_4$  group is made:



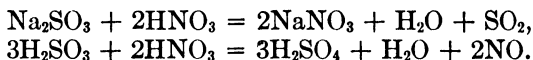
and a precipitate of  $\text{BaCO}_3$  will always be formed. The  $\text{Na}_2\text{CO}_3$  is removed by adding  $\text{HNO}_3$  and boiling:



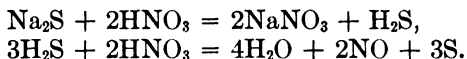
This addition of  $\text{HNO}_3$  results in the following complications when the tests for certain of the acid radicals are made:

(a) Any carbonate present in the original unknown will be decomposed by the boiling with  $\text{HNO}_3$ .

(b) Sulfites, if present, will to some extent be either decomposed or oxidized:



(c) Sulfides will to some extent either be driven off as  $\text{H}_2\text{S}$  or oxidized to sulfur:



Therefore, the solution prepared by boiling with  $\text{Na}_2\text{CO}_3$  will not give dependable tests for carbonates, sulfites, or sulfides. Furthermore, since  $\text{HNO}_3$  was used in its preparation, this solution cannot be used in testing for nitrates.

6. Because all the water-insoluble barium salts except  $\text{BaSO}_4$  are soluble in strong acids, it is imperative that the solution not be acid when  $\text{BaCl}_2$  is added. Accordingly, the solution is first made alkaline with  $\text{NH}_4\text{OH}$ . This will precipitate, as insoluble hydroxides, those cations whose hydroxides are insoluble in the presence of excess  $\text{NH}_4\text{OH}$ .

### Questions

1. List the anions whose solid salts show distinctive reactions when treated with concentrated  $\text{H}_2\text{SO}_4$ . Write the equations for the reactions and point out what is observed to take place in each case.

2. How would treatment with concentrated  $\text{H}_2\text{SO}_4$  enable you to distinguish between the following pairs of dry salts?

- a.  $\text{BaSO}_4$  and  $\text{Pb}(\text{NO}_3)_2$
- b.  $\text{KCl}$  and  $\text{Na}_3\text{AsO}_4$
- c.  $\text{MnSO}_3$  and  $\text{Na}_2\text{CO}_3$
- d.  $\text{NaC}_2\text{H}_3\text{O}_2$  and  $\text{NaCl}$

- e.  $\text{MgBr}_2$  and  $\text{K}_3\text{PO}_4$
- f.  $\text{CaCrO}_4$  and  $\text{KI}$
- g.  $\text{ZnS}$  and  $\text{Ba}(\text{BO}_2)_2$
- h.  $\text{KBr}$  and  $\text{KNO}_3$

3. A solid unknown is a mixture of the following compounds:  $\text{ZnCO}_3$ ,  $\text{Cu}_3(\text{PO}_4)_2$ ,  $\text{Pb}(\text{BO}_2)_2$ ,  $\text{MnSO}_3$ , and  $\text{NiS}$ . Write equations to show what happens when a solution is prepared as directed in Procedure 46(C).

4. In making a solution of a water-insoluble solid, why dissolve by boiling with  $\text{Na}_2\text{CO}_3$ ? Why not simply dissolve the solid in  $\text{HNO}_3$  and use this acid solution for making the group test for anions?

5. A mixture of salts was readily and completely soluble in cold water. Separate samples of this water solution gave no precipitate with  $\text{AgNO}_3$  or with  $\text{NH}_4\text{OH}$  and  $\text{BaCl}_2$ . What anions could be present in this salt mixture?

6. A mixture of barium and silver salts was readily and completely soluble in cold water. What anions can you be very sure are not present in this mixture?

## CHAPTER 9

### Specific Tests for Anions

THE THREE preliminary tests discussed in Chapter 8 may show the absence of certain anions and the presence of others. Information gained in the course of the cation analysis, together with information gained from observation of the solubility of the solid in water, may further establish the presence or absence of certain anions. For each salt mixture, however, there usually are several anions whose presence or absence is not established by any of the procedures noted above. Specific tests must then be carried out for each of them. Such specific tests are discussed in the present chapter in Procedures 32 to 44.

These specific tests are independent of the metallic ion analysis and in general can be made whether or not the tests for cations are carried out. They make it possible to test for nitrate in a fertilizer or for a phosphate in a baking powder without going through the systematic cation analysis.

In order that the student may become familiar with these specific tests before they are used in the analysis of salts and salt mixtures, the following experiment should be performed before the first salt or salt mixture is analyzed.

**Experiment 4: The specific tests for the anions.** Use solutions of the sodium salts of each of the 13 acids or a small amount of a solid salt of each of these acids. Carry out a specific test for each acid as directed in Procedures 32 to 44.

Note exactly what happens in each test and compare your observations with those noted in each procedure. Have each test observed and approved by your instructor. In the spaces below, write the equations for the reactions that take place in each specific test. Have these equations approved by your instructor before proceeding with the analysis of your first salt or mixture of salts.

$\text{AsO}_4^{3-}$  \_\_\_\_\_

$\text{PO}_4^{3-}$  \_\_\_\_\_

$\text{BO}_2^-$  or  $\text{BO}_3^{3-}$  \_\_\_\_\_

$\text{CrO}_4^{2-}$  \_\_\_\_\_

$\text{SO}_4^{2-}$  \_\_\_\_\_

$\text{SO}_3^{2-}$  \_\_\_\_\_

$\text{CO}_3^{2-}$  \_\_\_\_\_

$\text{S}^{2-}$  \_\_\_\_\_

$\text{I}^-$  \_\_\_\_\_

$\text{Br}^-$  \_\_\_\_\_

$\text{Cl}^-$  \_\_\_\_\_

$\text{NO}_3^-$  \_\_\_\_\_

$\text{C}_2\text{H}_3\text{O}_2^-$  \_\_\_\_\_

### SPECIFIC TESTS FOR ANIONS OF THE SULFURIC ACID GROUP

The order in which the specific tests for the anions of the sulfuric acid group should be performed is governed by the following facts. Arsenates, if present, will interfere with the test for phosphates and must be removed before the test for the phosphate ion can be made. Sulfites, if present, will interfere with the test for carbonates and must be removed before the carbonate test can be made. Consequently, the test for the sulfite must be made before the test for the carbonate ion, and the test for the arsenate must be made before the test for the phosphate ion. The order of performance of the tests for sulfate, borate, and chromate is not important.

#### **Procedure 32: Test for the arsenate ion ( $\text{AsO}_4^{3-}$ )**

(To be omitted if the cation analysis has proved the absence of arsenic.) Place 6–8 drops of the solution to be tested in a small test tube and add  $\text{Na}_2\text{CO}_3$  solution, dropwise and with constant stirring, until no more precipitation of metal carbonates takes place and the solution is no longer acidic. If a precipitate has formed, centrifuge and decant into a clean test tube, discarding any precipitate. Make the decantate acid with 1.5N HCl and boil to expel all  $\text{CO}_2$ . Then make just alkaline with 5N  $\text{NH}_4\text{OH}$ . If any precipitate forms, centrifuge and decant into a clean test tube, discarding the precipitate. Add 4–5 drops of magnesia mixture and mix thoroughly. If no precipitate forms, arsenate is absent. If a white precipitate forms, it may be  $\text{MgNH}_4\text{AsO}_4$  or  $\text{MgNH}_4\text{PO}_4$ , or both. Centrifuge and decant, and wash the precipitate three times with hot water. Add to the precipitate a drop of 0.25N  $\text{AgNO}_3$  solution. A chocolate-brown precipitate ( $\text{Ag}_3\text{AsO}_4$ ) proves the presence of arsenate. A yellow precipitate ( $\text{Ag}_3\text{PO}_4$ ) proves the presence of phosphate and, at the same time, proves the absence of arsenate.

## NOTES

1. The precipitate formed by magnesia mixture is not sufficient confirmation of the arsenate ion, since phosphates when present precipitate as  $\text{MgNH}_4\text{PO}_4$ , which looks exactly like the  $\text{MgNH}_4\text{AsO}_4$ . The addition of  $\text{AgNO}_3$  makes it possible to distinguish the arsenate from the phosphate.  $\text{AgNO}_3$  reacts with both  $\text{MgNH}_4\text{AsO}_4$  and  $\text{MgNH}_4\text{PO}_4$ , but  $\text{Ag}_3\text{AsO}_4$  is reddish brown and  $\text{Ag}_3\text{PO}_4$  is light yellow.

2. Magnesium ammonium arsenite ( $\text{MgNH}_4\text{AsO}_3$ ) is soluble and is not precipitated when magnesia mixture is added to a solution containing an arsenite. The decantate left after the removal of the  $\text{MgNH}_4\text{AsO}_4$  may contain  $\text{AsO}_3^{--}$ . If this decantate is made acid with  $\text{HCl}$  and  $\text{H}_2\text{S}$  passed into the solution, any  $\text{AsO}_3^{--}$  present will be precipitated as yellow  $\text{As}_2\text{S}_3$ .

3. Magnesia mixture is a solution containing  $\text{Mg}^{++}$ ,  $\text{OH}^-$ , and excess  $\text{NH}_4^+$ .  $\text{MgCl}_2$ ,  $\text{NH}_4\text{OH}$ , and  $\text{NH}_4\text{Cl}$  are common sources of these ions. The important reactions involved in the test for arsenate are



4. The addition of  $\text{Na}_2\text{CO}_3$  will precipitate out, as carbonates, all cations except sodium, potassium, and ammonium. These cations, if not removed as carbonates, would precipitate as insoluble arsenates, when the solution was made alkaline with  $\text{NH}_4\text{OH}$ . The arsenate ion would thus be lost. Traces of these cations not removed as carbonates would precipitate on addition of  $\text{NH}_4\text{OH}$ .

5. If an unknown substance contained arsenate, the cation analysis of that substance would give a positive test for arsenic in Procedure 13. If no positive test for arsenic was obtained in the cation analysis, arsenate could not have been present. Therefore, if arsenic has already been shown to be absent in the cation analysis, the test for the arsenate ion may be omitted. Performance of the test for arsenate will, however, serve as a check on the cation analysis.

**Procedure 33: Test for the phosphate ion ( $\text{PO}_4^{--}$ )**

(A) *If arsenates are absent.* Place 4–5 drops of the solution in a test tube, acidify with 3N  $\text{HNO}_3$ , add 3–4 drops of ammonium molybdate solution  $[(\text{NH}_4)_2\text{MoO}_4]$ , mix thoroughly, and heat almost to boiling. The formation of a finely divided



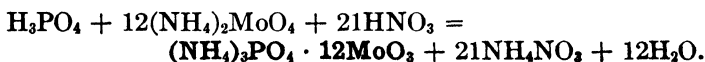
yellow precipitate  $[(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3]$  confirms the presence of the phosphate ion.

(B) *If arsenates are present.* Place a small bit of the solid in a test tube, add 7–8 drops of 12N HCl, and heat just to boiling. Treat with  $\text{H}_2\text{S}$  for about 20 seconds. Add 10 drops of water, mix thoroughly, centrifuge, and decant into a casserole. Evaporate to dryness but do not bake. Cool, and then add 5 drops of water and 5 drops of 3N  $\text{HNO}_3$ . Stir thoroughly and transfer to a test tube. If necessary, centrifuge and decant, discarding the precipitate. Treat the decantate with 3–4 drops of ammonium molybdate solution, mix thoroughly, and heat almost to boiling. A yellow precipitate  $[(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3]$  proves the presence of phosphate.

#### NOTES

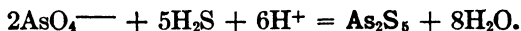
1. Both phosphates and arsenates react with ammonium molybdate to form insoluble yellow precipitates, ammonium phosphomolybdate  $[(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3]$  and ammonium arsenomolybdate  $[(\text{NH}_4)_3\text{AsO}_4 \cdot 12\text{MoO}_3]$ . As a consequence, arsenates must be removed before the confirmatory test for phosphates can be made.

2. The formation of the yellow precipitate,  $(\text{NH}_4)_3\text{PO}_4 \cdot 12\text{MoO}_3$ , takes place as follows:



Precipitation takes place most readily at a temperature of  $60^\circ$  in the presence of excess  $\text{HNO}_3$ .

3. Arsenates, if present, are removed as  $\text{As}_2\text{S}_5$  by precipitation with  $\text{H}_2\text{S}$ :



#### Procedure 34: Test for the borate ion ( $\text{BO}_3^{3-}$ or $\text{BO}_2^-$ )

Place a small quantity of the solid material in a casserole, add 3–4 drops of 36N  $\text{H}_2\text{SO}_4$ , and stir thoroughly. Then add 10–12 drops of methyl alcohol and again mix thoroughly; then set fire to the mixture. *Do not stir after the mixture has taken fire.* If it burns with a green flame the instant that it

takes fire, the borate ion is present. A green flame that does not appear until 20 or 30 seconds after the mixture has taken fire or unless the mixture is stirred while on fire is due to copper or barium and should be ignored.

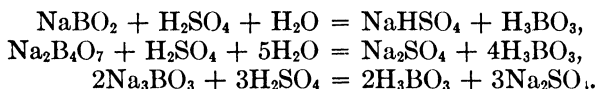
### NOTES

1. Copper and barium do not interfere with the borate test because their salts are not volatilized when the mixture *first takes fire*.

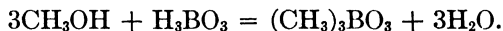
2. There are three boric acids: orthoboric ( $\text{H}_3\text{BO}_3$ , the boracic acid of commerce), metaboric ( $\text{HBO}_2$ ), and tetraboric ( $\text{H}_2\text{B}_4\text{O}_7$ ).

Of these, the  $\text{H}_3\text{BO}_3$  is the only one that is of importance. All three of these boric acids form stable salts.

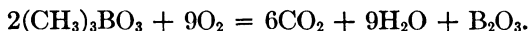
3. All borates react with  $\text{H}_2\text{SO}_4$  to form orthoboric acid,  $\text{H}_3\text{BO}_3$ :



In the presence of sulfuric acid,  $\text{H}_3\text{BO}_3$  reacts with alcohol to form the volatile ester, methyl borate,  $(\text{CH}_3)_3\text{BO}_3$ :



The methyl borate burns with a characteristic green flame, forming solid  $\text{B}_2\text{O}_3$  (boric acid anhydride):

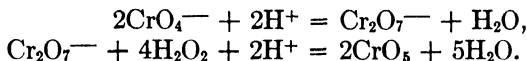


### Procedure 35: Test for the chromate ion ( $\text{CrO}_4^{--}$ )

(To be omitted if no chromium was found in the complete cation analysis.) Place two drops of the solution in a test tube, add 10 drops of water and make just acid with 3N  $\text{HNO}_3$ . Add 5–6 drops of ether and 1 drop of 3 per cent  $\text{H}_2\text{O}_2$ , shake well, and then allow to settle. A blue coloration of the ether layer confirms the presence of the chromate ion. If no blue color appears, add a second drop of  $\text{H}_2\text{O}_2$  and shake, then a third, up to 5 drops.

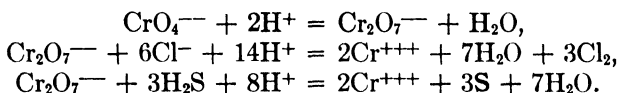
### NOTES

1. The blue coloration in the ether layer is due to the presence of chromium peroxide,  $\text{CrO}_5$ :



See Note 1, Procedure 21, for further details concerning this reaction.

2. If a chromate is carried through the complete cation analysis it is, in part at least, reduced to  $\text{Cr}^{+++}$  when the solution is evaporated down with 6N HCl in Procedure 5 and is completely reduced to  $\text{Cr}^{+++}$  when the sulfides of the copper-arsenic group are precipitated in Procedure 5:



The resulting  $\text{Cr}^{+++}$  ions remain in the decantate from Procedure 5 and are subsequently precipitated as  $\text{Cr}(\text{OH})_3$  in Procedure 15. A positive test for chromium is then obtained in Procedure 21.

The fact that a positive test for chromium is obtained in Procedure 21 does not mean, however, that the particular salt mixture contained chromate. The chromium may have been present as a  $\text{Cr}^{+++}$  salt,  $\text{CrCl}_3$  for instance.

### Procedure 36: Test for the sulfate ion ( $\text{SO}_4^{--}$ )

Place a few drops of the solution in a test tube, acidify with 6N HCl, and then add a drop of N  $\text{BaCl}_2$ . A white precipitate ( $\text{BaSO}_4$ ) proves the presence of sulfate.

### NOTES

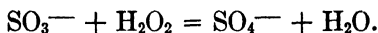
1. A trace of sulfate may be present as an impurity in the reagent.
2. Sulfites are slowly oxidized to sulfates by atmospheric oxygen. Consequently, sulfites commonly show a positive test for sulfates.

### Procedure 37: Test for the sulfite ion ( $\text{SO}_3^{--}$ )

Place 7–8 drops of the solution in a test tube, acidify with 6N HCl, add 2–3 drops of N  $\text{BaCl}_2$ , and mix thoroughly. If a precipitate ( $\text{BaSO}_4$ ) forms, remove it by centrifuging and decanting. To the clear decantate add a drop of 3 per cent  $\text{H}_2\text{O}_2$ . The formation of a white precipitate ( $\text{BaSO}_4$ ) proves the presence of sulfite.

## NOTES

1. The  $\text{H}_2\text{O}_2$  oxidizes the sulfite to sulfate:



The barium ions in solution react with these sulfate ions to form insoluble  $\text{BaSO}_4$ .

2. Any sulfate ions in solution are first removed as barium sulfate.

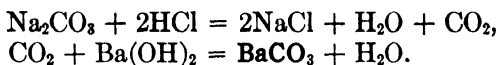
**Procedure 38: Test for the carbonate ion ( $\text{CO}_3^-$ )**

(A) *When sulfites are absent.* Place a small amount of the solid in a test tube. Then add a few drops of 6N HCl. Test the escaping gas for  $\text{CO}_2$  by holding a drop of barium hydroxide solution, suspended from the tip of a medicine dropper, a short distance down into the mouth of the test tube. The "clouding" of the drop, due to the formation of a white precipitate of barium carbonate ( $\text{BaCO}_3$ ), proves the presence of carbonate.

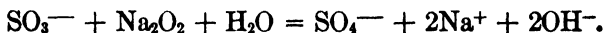
(B) *When sulfites are present.* Place a small amount of the solid in a test tube and add an equal amount of solid  $\text{Na}_2\text{O}_2$ . Then add 3–4 drops of water and mix thoroughly. Then proceed as directed in the second sentence of (A).

## NOTES

1. Carbonates react with acids to evolve  $\text{CO}_2$  gas. This  $\text{CO}_2$  reacts with  $\text{Ba}(\text{OH})_2$  solution to form a white precipitate of  $\text{BaCO}_3$ :



2. Sulfites evolve  $\text{SO}_2$  gas when treated with acids. The  $\text{SO}_2$  gas will react with  $\text{Ba}(\text{OH})_2$  solution to form a white precipitate of  $\text{BaSO}_3$ , exactly as does  $\text{CO}_2$ . Sulfites must therefore be removed or destroyed before the test for carbonates is carried out. Sodium peroxide oxidizes sulfites to sulfates:



## SPECIFIC TESTS FOR ANIONS OF THE HYDROCHLORIC ACID GROUP

### HYDROCHLORIC ACID GROUP

Sulfide, bromide, and iodide ions will interfere with the specific test for chlorides. Iodide ions will interfere with the specific test for bromides. For these reasons the specific tests for the anions of the hydrochloric acid group should be made in the following order: sulfides, iodides, bromides, and chlorides.

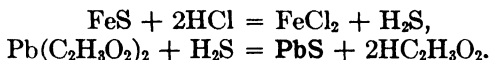
#### **Procedure 39: Test for the sulfide ion ( $S^{2-}$ )**

Place a small quantity of the solid in a test tube and add 10 drops of 6N HCl. Hold a strip of filter paper moistened with  $Pb(C_2H_3O_2)_2$  solution over the mouth of the test tube so that any gas that is being evolved will come in contact with the lead acetate. A brownish-black stain (**PbS**) on the paper confirms the presence of sulfides.

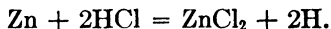
If no blackening of the lead acetate occurs after 1 minute, heat the tube gently; if still no reaction occurs, add a small amount of granulated zinc to the contents of the tube. If the lead acetate is not darkened, the sulfide ion is absent; if it is darkened, sulfide is present.

#### NOTES

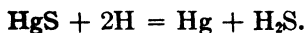
1. The reactions that take place in the test for sulfides are:



2. The sulfides of nickel and cobalt and the metals of the silver and copper-arsenic groups are not soluble in dilute HCl. When zinc is added, however, hydrogen is liberated:



The hydrogen reduces the sulfides,  $H_2S$  being evolved.

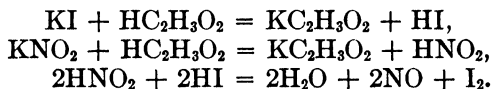


**Procedure 40: Test for the iodide ion ( $I^-$ )**

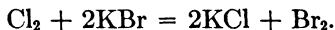
Place 5 drops of the solution in a test tube and acidify with 5N  $HC_2H_3O_2$ . Then add 2 drops of N  $KNO_2$ . A reddish-brown coloration, due to the liberation of iodine, proves the presence of iodide. If the brown color is very faint add a few drops of carbon tetrachloride ( $CCl_4$ ) and shake. A violet coloration in the  $CCl_4$  layer shows the presence of iodine.

**NOTES**

1. Nitrous acid ( $HNO_2$ ) will oxidize HI to give free  $I_2$  but it will not oxidize HBr or HCl, so that this test can be made in the presence of chlorides and bromides:



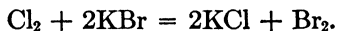
2. The water layer from which  $I_2$  has been extracted by the  $CCl_4$  can be tested for the bromide ion as follows: Pour off the colorless supernatant water solution, add a few drops of chlorine water, and shake with  $CCl_4$ . If bromides are present, bromine will be liberated and will color the  $CCl_4$  brown:

**Procedure 41: Test for the bromide ion ( $Br^-$ )**

(Iodides will interfere with this test.) Place 5 drops of the solution in a test tube; add 2-3 drops of  $CCl_4$  and 5 drops of chlorine water. Shake and allow to settle. A brownish-yellow color to the  $CCl_4$  shows that bromine has been liberated and proves the presence of the bromide ion.

**NOTES**

1. Chlorine will liberate bromine from a bromide:



This bromine is more soluble in  $CCl_4$  than it is in water.

If iodides are present, free iodine would be liberated and would cover up the color of the bromine. Consequently, iodides must be

removed by oxidation with nitrite before the test for bromides can be made (see Notes 1 and 2, Procedure 40).

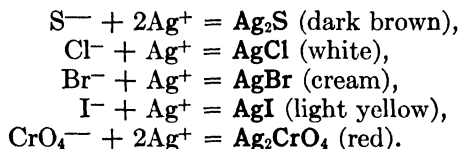
2. For methods used to detect iodides, bromides, and chlorides in mixtures of two or three of these ions, the student is referred to Note 2, Procedure 42.

### Procedure 42: Test for the chloride ion ( $\text{Cl}^-$ )

(Sulfides, bromides, and iodides will interfere with this test.) Place 5–6 drops of the solution in a test tube, acidify with 3N  $\text{HNO}_3$ , and add a drop of 0.25N  $\text{AgNO}_3$ . A white, curdy precipitate ( $\text{AgCl}$ ) proves the presence of chlorides.

### NOTES

1. Since the other members of the hydrochloric acid group precipitate with  $\text{AgNO}_3$  in acid solution, this test is not conclusive unless  $\text{S}^-$ ,  $\text{Br}^-$ , and  $\text{I}^-$  are definitely shown to be absent. Chromate ions, if present in high concentrations, may also interfere:



Interference from chromate ions can be eliminated by dilution with 3N  $\text{HNO}_3$ .

Sulfide ions can be removed by boiling the solution with dilute  $\text{H}_2\text{SO}_4$  until the escaping vapors give no test for  $\text{H}_2\text{S}$  gas with filter paper moistened with lead acetate solution.

Iodide and bromide ions are eliminated as described in Note 2.

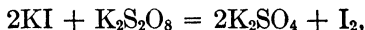
2. *Separation and detection of chlorides, bromides, and iodides in the presence of one another.* Place 15 drops of the solution in a casserole, add 15 drops of 5N  $\text{HC}_2\text{H}_3\text{O}_2$  and 30 drops of water, and mix thoroughly. Then add a small quantity of solid potassium persulfate ( $\text{K}_2\text{S}_2\text{O}_8$ ) and heat. A brown coloration, due to the liberation of iodine, proves the presence of iodide.

Boil the solution until all of the iodine is removed, replenishing the liquid with water. Now add 15 drops of 4N  $\text{H}_2\text{SO}_4$  and another small quantity of  $\text{K}_2\text{S}_2\text{O}_8$  and heat to boiling. A brown coloration, due to bromine, proves the presence of bromides.

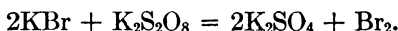
Boil the solution until all of the bromine is driven off, replacing the liquid with water. Cool, acidify with 3N  $\text{HNO}_3$ , and add 2–3

drops of 0.25N  $\text{AgNO}_3$ . A white precipitate ( $\text{AgCl}$ ) proves the presence of chlorides.

This separation depends on the fact that, in acetic acid solution,  $\text{K}_2\text{S}_2\text{O}_8$  will oxidize iodide but will not oxidize bromide or chloride:



whereas in a more strongly acid solution it will oxidize iodide and bromide but will not oxidize chloride:



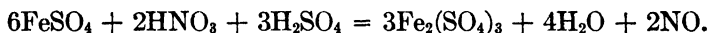
For additional methods for detecting the halides in the presence of one another, the student is referred to the textbooks listed at the end of Chapter 2.

#### Procedure 43: Test for the nitrate ion ( $\text{NO}_3^-$ )

(In the absence of iodides, bromides, and chromates.) Place 2 drops of the water solution, or the supernatant liquid obtained by treating the solid with hot water, in a test tube and add 10 drops of 36N  $\text{H}_2\text{SO}_4$ . Mix thoroughly and cool. Carefully add 3–4 drops of  $\text{FeSO}_4$  solution, allowing the latter to float on top of the sulfuric acid solution. Allow to stand for one or two minutes. A brown coloration ( $\text{FeSO}_4 \cdot \text{NO}$ ) at the junction of the two layers proves the presence of nitrate.

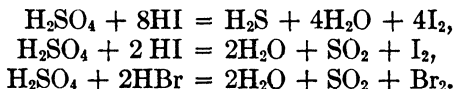
#### NOTES

1. The test for the nitrate ion is based upon the fact that in the presence of concentrated  $\text{H}_2\text{SO}_4$ ,  $\text{FeSO}_4$  reduces  $\text{HNO}_3$  to NO:



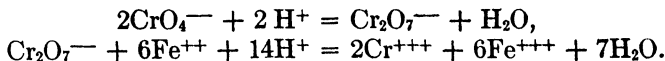
The NO formed combines with excess  $\text{FeSO}_4$  to form the characteristic brown compound,  $\text{FeSO}_4 \cdot \text{NO}$ . This compound decomposes upon heating; hence the test must be made at room temperatures.

2. Iodides and bromides react with concentrated  $\text{H}_2\text{SO}_4$  to liberate  $\text{I}_2$  and  $\text{Br}_2$ :



Chromates, if present, will be reduced by  $\text{Fe}^{++}$  to green  $\text{Cr}^{+++}$ :





The colors of  $\text{I}_2$ ,  $\text{Br}_2$ , and  $\text{Cr}^{+++}$  will interfere with the detection of the brown color of  $\text{FeSO}_4 \cdot \text{NO}$ . Consequently,  $\text{I}^-$ ,  $\text{Br}^-$ , and  $\text{CrO}_4^{--}$  must be removed as follows: Place 4 drops of the water solution in a test tube and add N  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  until precipitation is complete. Centrifuge and decant, discarding the precipitate. Treat the decantate with silver sulfate solution until precipitation is complete. Centrifuge and decant, into a casserole, discarding the precipitate. Evaporate the solution down to a volume of about 2 drops, add 2 drops of water, and transfer to a test tube. Test this solution for nitrate according to Procedure 43.

3. Since all nitrates are soluble in water, the nitrate ions will be contained in the supernatant liquid obtained by digesting the solid material with water, even though the solid may not be completely soluble.

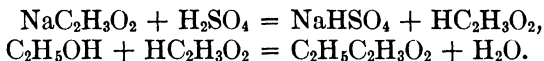
#### Procedure 44: Test for the acetate ion ( $\text{C}_2\text{H}_3\text{O}_2^-$ )

Place a small amount of the solid in a test tube, add 2-3 drops of 36N  $\text{H}_2\text{SO}_4$ , and mix thoroughly (see Note 1). Add 4 drops of ethyl alcohol ( $\text{C}_2\text{H}_5\text{OH}$ ) and again mix thoroughly. Warm gently but do not boil, warming the entire length of the tube. Carefully smell the odor of the escaping fumes. A fruity odor, due to ethyl acetate ( $\text{C}_2\text{H}_5\text{C}_2\text{H}_3\text{O}_2$ ), proves the presence of acetate.

#### NOTES

1. If sulfites, carbonates, iodides, bromides, chlorides, or sulfides are present, the mixture should be warmed gently for some time after addition of the sulfuric acid and before addition of the alcohol. This heating will drive off all  $\text{SO}_2$ ,  $\text{CO}_2$ ,  $\text{I}_2$ ,  $\text{Br}_2$ ,  $\text{HCl}$ , and  $\text{H}_2\text{S}$ . If they are not driven off, their odors will mask the characteristic odor of the ethyl acetate. Care should be taken so that the heating is not so intense that  $\text{HC}_2\text{H}_3\text{O}_2$  is distilled off.

2. When an acetate is treated with concentrated  $\text{H}_2\text{SO}_4$ , acetic acid is liberated. This acetic acid reacts with ethyl alcohol to form the volatile ester,  $\text{C}_2\text{H}_5\text{C}_2\text{H}_3\text{O}_2$ ; the characteristic fruity odor of the latter compound makes possible its identification:



3. The presence of acetate is shown in the preliminary treatment with sulfuric acid (Procedure 29), in which it gives the characteristic odor of vinegar (acetic acid).

4. When a solid acetate is heated in a test tube at a fairly high temperature, charring takes place, the material turns black, and the characteristic acrid odor of burned hair is given off. Charring on heating is characteristic of the salts of organic acids. Since acetic acid is the only organic acid among the 13, the incidence of charring when the solid is heated is proof of the presence of acetate.

5. Because the identification of acetates depends, in each of the tests referred to, on a characteristic odor (the fruity odor of  $\text{C}_2\text{H}_5\text{C}_2\text{H}_3\text{O}_2$ , the vinegar odor of  $\text{HC}_2\text{H}_3\text{O}_2$ , and the acrid, burned-hair odor of the charred residue) and because these odors are easily masked by the  $\text{SO}_2$ ,  $\text{I}_2$ ,  $\text{Br}_2$ ,  $\text{HCl}$ , and  $\text{H}_2\text{S}$ , which may be liberated when concentrated  $\text{H}_2\text{SO}_4$  is added to a dry salt or even when the proper combination of dry salts is heated, the detection of acetate leaves much to be desired. Of the three tests, the charred odor which results when an acetate is heated is the least liable to be obscured by other odors; unfortunately, it is the most difficult odor to detect. It very often happens, however, that the final detection of acetate must depend on the observation of charring when the solid is heated in a test tube.

6. Since all acetates are soluble, one cannot fall back on precipitation reactions for the detection of acetate ions.

### Questions

- Write equations for the reactions that take place in the specific tests for each of the 13 anions.
- Describe the method by which you would make a specific test for:
  - $\text{NO}_3^-$  in an unknown which contains  $\text{I}^-$ .
  - Borate in an unknown which contains  $\text{Cu}^{++}$ .
  - $\text{CO}_3^{--}$  in an unknown which contains  $\text{SO}_3^{--}$ .
  - $\text{PO}_4^{--}$  in an unknown which contains  $\text{AsO}_4^{--}$ .
  - $\text{Br}^-$  in an unknown which contains  $\text{I}^-$ .
  - $\text{Cl}^-$  in an unknown which contains  $\text{S}^{--}$ .
  - $\text{SO}_3^{--}$  in an unknown which contains  $\text{SO}_4^{--}$ .
  - $\text{C}_2\text{H}_3\text{O}_2^-$  in an unknown which contains  $\text{SO}_3^{--}$ .
  - $\text{NO}_3^-$  in an unknown which contains  $\text{CrO}_4^{--}$ .
  - $\text{AsO}_4^{--}$  in an unknown which contains  $\text{PO}_4^{--}$ .

3. Describe the method by which you would test for:
- Boric acid in an eyewash.
  - Nitrate in a solid fertilizer.
  - Phosphate in bath salts.
  - Carbonate in limestone.
  - Arsenate in an insecticide.
  - Sulfite in a bleaching solution.
  - Iodide in table salt.

## CHAPTER 10

### The Analysis of Salts and Salt Mixtures

*To the student:* It is important that the complete picture of just how you go about analyzing a salt or salt mixture be clearly in mind before you start analyzing your first salt. Therefore, read this entire chapter carefully before starting your first salt analysis.

The analysis of a salt or mixture of salts calls for the detection of both anions and cations. To accomplish this, what is done, essentially, is to run a complete analysis for anions according to Chapters 8 and 9 and a complete cation analysis according to Chapters 3, 4, 5, and 6. In order to carry out these analyses, it is first necessary to put the material into solution; and in order to know something about the solid material itself one very naturally examines it carefully to see exactly what it looks like.

The analysis of a salt or salt mixture resolves itself, therefore, into four steps:

- (1) The physical examination of the solid.
- (2) The selection of the proper solvent.
- (3) The analysis for cations.
- (4) The analysis for anions.

The procedure by which these steps are carried out and the manner in which the information gained in one step is used to augment information gained in another step will be presented in this chapter. The four steps will be discussed in the order listed above, which, however, need not necessarily always be followed. If a mixture is soluble in water it usually is advantageous to run the anion analysis before the cation analysis. On the other hand, if the mixture is insoluble in water it is usually best to do the cation analysis first.

## PHYSICAL EXAMINATION OF THE SOLID

Certain metals, such as copper, nickel, manganese, chromium, cobalt, and iron form colored salts. Others form white salts. Certain anions, such as chromates, dichromates, and permanganates, have characteristic colors. It is important, therefore, to note the color of the solid, since it may give indications of the presence of one or more of the ions listed above.

The more common characteristic colors are:

$\text{CrO}_4^{--}$ , yellow.

$\text{Cr}^{+++}$ , green.

$\text{Cr}_2\text{O}_7^{--}$ , orange red.

$\text{Cu}^{++}$ , blue to green.

$\text{MnO}_4^-$ , violet purple.

$\text{Co}^{++}$ , wine red to blue.

$\text{Ni}^{++}$ , green.

$\text{Mn}^{++}$ , pink.

$\text{Fe}^{+++}$ , reddish brown to yellow.

### Procedure 45: Physical examination of the sample

Examine the unknown carefully, noting the color or colors, and whether the material is crystalline or noncrystalline, homogeneous or heterogeneous. Record your observations on a report blank on pages 181–188.

### NOTES

1. The information gained by the examination of the solid may not, by itself, be of much value in the analysis of a sample. However, when combined with the entire body of information, it may prove to be very valuable. The fact that a solid is green is of itself of some value; when combined with the fact that the solid is soluble in water, the fact of its green color becomes, as will be pointed out later, extremely valuable.

2. The fact that the sample is white does not prove the absence of all ions that usually form colored salts. Anhydrous copper sulfate is white, and so is ferric phosphate. The salts with characteristic colors, moreover, may be present in such small amounts as to be covered up by an excess of other salts.

## SELECTION OF THE SOLVENT

Before a solid can be analyzed, it must be dissolved. The choice of solvent is made by testing the solubility of a portion

of the solid in various solvents. Water is the most desirable solvent; the water solution can be used for all procedures except those which specifically call for the use of some of the solid. If the solid is insoluble in water, two separate solutions should be prepared, one for cation analysis, the other for anion analysis. The solution for cation analysis should be prepared by dissolving the solid in hydrochloric acid. The solution for anion analysis should be prepared by boiling with sodium carbonate.

#### **Procedure 46: Dissolving the solid**

(A) Test a bit of the solid with 20 drops of water, first cold, then hot, to see if it will dissolve. If it is completely dissolved, prepare a stock solution by dissolving a quantity the volume of two drops of water in 5 cc. of water and use this solution for cation analysis, preliminary tests for anions, and specific tests for anions.

(B) If the solid is not soluble in water, prepare a solution for cation analysis by dissolving in HCl or HNO<sub>3</sub>, or, if necessary, in aqua regia (see Procedure 28). First try 6N HCl, then 12N HCl, followed by dilution with an equal volume of hot water; then try 16N HNO<sub>3</sub>, followed by dilution with water; finally try aqua regia (see Note 1).

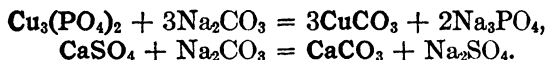
(C) If the solid is not soluble in water prepare a solution for anion analysis as follows (see Notes 11 and 12). Place in a casserole a quantity of the solid the volume of two drops of water; then add 5 cc. of a saturated solution of Na<sub>2</sub>CO<sub>3</sub> and boil gently for two minutes. Transfer to test tubes, centrifuge, and decant, discarding the precipitates (carbonates of metals) (see Note 1). Place the decantate in a casserole, make just acid with 3N HNO<sub>3</sub>, and boil gently until all CO<sub>2</sub> has been driven off.

#### **NOTES**

1. If the solid is insoluble in aqua regia it will be necessary to prepare a solution for cation analysis by boiling with sodium carbonate

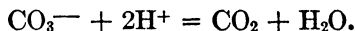
as directed in Procedure 46(C). The metals will be precipitated as carbonates. The precipitate of the metal carbonates must therefore be saved, washed three times with hot water, and then dissolved in 6N HCl. This series of steps gives a solution of metal chlorides.

2. The following reaction takes place when a water-insoluble salt, such as  $\text{Cu}_3(\text{PO}_4)_2$  or  $\text{CaSO}_4$ , is boiled with a solution of sodium carbonate:



The excessive amount of  $\text{Na}_2\text{CO}_3$  causes both reactions to be quite complete to the right. This means that the anions,  $\text{PO}_4^{--}$  and  $\text{SO}_4^{--}$ , are in solution as their soluble sodium salts, whereas the cations,  $\text{Cu}^{++}$  and  $\text{Ca}^{++}$ , are precipitated as insoluble carbonates. Since the solution being prepared is to be used for anion analysis, the fact that the cations are left behind in the precipitate is of no concern. The important thing is that the anions are in solution as their sodium salts.

The solution is boiled with  $\text{HNO}_3$  to remove the excess carbonate:

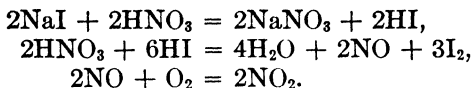


3. Sulfides will yield a precipitate of sulfur when dissolved in aqua regia. This sulfur should be discarded.

4. The reactions that take place when a solid is dissolved in acid may give definite information about the presence or absence of certain ions. Carbonates, sulfites, and some sulfides give off  $\text{CO}_2$ ,  $\text{SO}_2$ , and  $\text{H}_2\text{S}$  gas, respectively. Chromates change in color from yellow to orange red. When effervescence occurs, the odor of the gas evolved often gives valuable clues about the anions present.

5. The evolution of chlorine gas when a solid is dissolved in concentrated HCl shows the presence of some oxidizing agent such as a nitrate, a chromate, a dioxide, or a peroxide.

6. The evolution of  $\text{I}_2$ ,  $\text{Br}_2$ , or  $\text{Cl}_2$  when a substance is dissolved in concentrated  $\text{HNO}_3$  shows the presence of iodides, bromides, or chlorides:

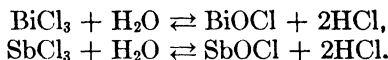


7. The evolution of brown fumes of  $\text{NO}_2$  when a substance is dissolved in  $\text{HNO}_3$  shows the presence of reducing agents such as sulfides, sulfites, iodides, or bromides.

8. Many chlorides such as  $\text{NaCl}$  and  $\text{BaCl}_2$ , though soluble in

water, are not dissolved by concentrated HCl. Hence the directions to dilute the solution with water after heating with hot concentrated acids.

9. Bismuth and antimony salts hydrolyze strongly in water to give the insoluble basic salts:



The basic salts are readily dissolved by excess of acids.

10. Concentrated  $\text{HNO}_3$ , because of its powerful oxidizing property, dissolves many metallic sulfides that are unattacked by HCl. Sulfur is usually liberated.

11. It will not always be necessary or wise to prepare a solution of a water-insoluble mixture for anion analysis as directed in Procedure 46(C). Suppose, for instance, that the treatment with concentrated sulfuric acid (Procedure 29) shows the absence of all anions except  $\text{SO}_4^{--}$ ,  $\text{PO}_4^{--}$ ,  $\text{AsO}_4^{--}$ , and  $\text{BO}_2^-$ , whereas the cation analysis shows the absence of  $\text{AsO}_4^{--}$ . Specific tests for  $\text{SO}_4^{--}$ ,  $\text{PO}_4^{--}$ , and  $\text{BO}_2^-$  can then be carried out on the solid or on solutions prepared with dilute  $\text{HNO}_3$  according to Procedure 46(B). The preliminary tests with  $\text{AgNO}_3$  and  $\text{BaCl}_2$  (Procedures 30 and 31) can be omitted entirely. The same reasoning will hold if the sulfuric acid treatment (Procedure 29) shows the absence of all anions except  $\text{CO}_3^{--}$ ,  $\text{SO}_4^{--}$ ,  $\text{PO}_4^{--}$ ,  $\text{AsO}_4^{--}$ , and  $\text{BO}_2^-$ .

12. A solution for use in anion analysis can be prepared by dissolving the solid mixture in nitric acid. If such a solution is prepared, its use will involve the following limitations:

(a) When such a solution is treated with  $\text{AgNO}_3$  in Procedure 30 the only insoluble silver salts that could precipitate are  $\text{AgCl}$ ,  $\text{AgBr}$ ,  $\text{AgI}$ ,  $\text{Ag}_2\text{S}$ , and  $\text{Ag}_2\text{CrO}_4$ . All other silver salts are soluble in  $\text{HNO}_3$ .

(b) When such a solution is treated with  $\text{BaCl}_2$  in Procedure 31 it must not first be made alkaline with  $\text{NH}_4\text{OH}$ . The only insoluble barium salt that could then precipitate is  $\text{BaSO}_4$ ; all other barium salts are soluble in  $\text{HNO}_3$ .

Obviously, then, if such a nitric acid solution is used,  $\text{SO}_3^{--}$ ,  $\text{CO}_3^{--}$ ,  $\text{PO}_4^{--}$ ,  $\text{AsO}_4^{--}$ , and  $\text{BO}_2^-$  must be eliminated or verified either by cation analysis, by sulfuric acid treatment (Procedure 29), or by specific tests. Since  $\text{SO}_3^{--}$  and  $\text{CO}_3^{--}$  are either eliminated or indicated by sulfuric acid treatment and  $\text{AsO}_4^{--}$  would be detected in the cation analysis, the only anions that would always require elimination or detection by specific tests are  $\text{PO}_4^{--}$  and  $\text{BO}_2^-$ .

13. Some solids must be fused with sodium carbonate in order to



prepare a solution for analysis. Directions for carrying out such a fusion are given in the references listed at the end of Chapter 2.

### ELIMINATION OF ANIONS AND CATIONS ON THE BASIS OF SOLUBILITY

After the sample to be analyzed has been dissolved in an appropriate solvent, the next step would be to go through a complete cation analysis according to Procedures 1-27 and follow it with a complete anion analysis according to Procedures 29-44. In most analyses that is exactly what is done. In some instances, however, observations of specific behavior may make it possible to eliminate certain cations or anions and thereby modify and shorten the over-all procedure.

To illustrate, suppose a salt mixture dissolves readily and completely in cold water to give a green solution. A green solution means the presence of either copper, nickel, or chromium. The mixture cannot, therefore, contain carbonates, sulfites, phosphates, borates, chromates, or sulfides, since these anions all form insoluble salts with copper, nickel, and chromium. The preliminary test for anions involving treatment of the solution with  $\text{BaCl}_2$  can be omitted, since all but one of the anions detected by this test are already eliminated.

In another illustration a salt mixture dissolves in water to give a yellow solution. This solution turns orange when  $\text{HCl}$  is added in the first step in Procedure 1. Such behavior clearly indicates the presence of a chromate. Since the chromates of all metals except magnesium, sodium, potassium, and ammonium are insoluble, there is no need to test for any cations except these four.

In another case a salt mixture dissolves readily and completely in cold water to give a water-clear solution. When  $\text{HCl}$  is added in the first step in Procedure 1, vigorous effervescence takes place, a colorless, odorless gas being evolved. Such behavior clearly indicates the presence of carbonate; and since sodium, potassium, and ammonium alone form soluble carbonates, they are the only cations that can be present.

In still another case a student first does the anion analysis on a water-soluble mixture and finds nitrates, chlorides, and phosphates. Sodium, potassium, and ammonium are the only cations whose nitrates, chlorides, and phosphates are all soluble. A complete cation analysis was therefore unnecessary in this case.

Eliminations such as those cited above require a knowledge of the solubilities of the salts of the various acids. The rules governing the solubility of the common salts are given below.

### THE SOLUBILITY RULES

1. The nitrates, chlorates, and acetates of all metals are soluble in water.

2. All sodium, potassium, and ammonium salts are soluble in water.

3. The chlorides, bromides, and iodides of all metals except lead, silver, and univalent mercury are soluble in water.  $\text{HgI}_2$  is insoluble in water.  $\text{PbCl}_2$ ,  $\text{PbBr}_2$ , and  $\text{PbI}_2$  are soluble in hot water. The water-insoluble chlorides, bromides, and iodides are also insoluble in dilute acids.

4. The sulfates of all metals except lead, mercurous mercury, barium, and calcium are soluble in water. Silver sulfate is slightly soluble. The water-insoluble sulfates are also insoluble in dilute acids.

5. The carbonates, phosphates, borates, sulfites, chromates, and arsenates of all metals except sodium, potassium, and ammonium are insoluble in water but soluble in dilute acids.  $\text{MgCrO}_4$  is soluble in water;  $\text{MgSO}_3$  is very slightly soluble in water.

6. The sulfides of all metals except barium, calcium, magnesium, sodium, potassium, and ammonium are insoluble in water.

7. The hydroxides of sodium, potassium, and ammonium are very soluble in water. The hydroxides of calcium and barium are moderately soluble. The oxides and hydroxides of all other metals are insoluble.

## NOTES

1. The solubility rules given above refer only to the metals and acid radicals discussed in this course.

2. Bismuth, antimony, tin, and mercuric salts hydrolyze in neutral or weakly acid solutions to give the basic salts. These basic salts are soluble in dilute acids but are not soluble in water.

3. Solutions of ferric, lead, tin, mercuric, copper, and aluminum salts, when boiled, often hydrolyze to give precipitates of the hydroxides or basic salts of these metals.

### HOW TO USE SOLUBILITY RULES TO ELIMINATE ACID RADICALS

The use of these solubility rules as an aid in the elimination of acid radicals can best be illustrated by a few concrete examples.

*Example 1:* The sample is readily and completely soluble in cold water. Lead is the only metallic ion that was found in the cation analysis.

*Conclusion:* Nitrates and acetates may be present because the nitrates and acetates of all metals are soluble (Rule 1).

All other acid radicals must be absent because they all form lead salts which are insoluble in water (Rules 3, 4, 5, 6, and 7).

It is therefore necessary to test for nitrate and acetate.

*Example 2:* The solid is readily soluble in water; zinc is the only metal present.

*Conclusion:*

Nitrates and acetates may be present (Rule 1).

Sulfates may be present (Rule 4).

Chlorides, bromides, and iodides may be present (Rule 3).

Sulfites, carbonates, phosphates, borates, arsenates, chromates, and sulfides cannot be present (Rules 5 and 6).

All anions except acetates, nitrates, sulfates, chlorides, bromides, and iodides are therefore eliminated because the salt is soluble in cold water and contains zinc as the only metallic ion.

*Example 3:* The solid is completely soluble in cold water, and sodium is the only cation present.

No acids can be eliminated because, according to Rule 2, sodium forms soluble salts with all acids. (Chromates and arsenates are absent because chromium and arsenic were not found in the course of the metal analysis).

*Example 4:* The solid is readily and completely soluble in cold water; barium, silver, and sodium ions are present.

Any anion which forms an insoluble salt with one or more of the above cations is eliminated. Therefore, the only possible anions are nitrate and acetate, since they are the only anions that form soluble salts with all three cations (Rule 1).

It may be reasoned that, since the unknown contains  $\text{Na}^+$  and since all sodium salts are soluble, all acids may be present. To show the incorrectness of this reasoning, let us assume that we are dissolving in water a mixture of the three soluble salts  $\text{Na}_2\text{SO}_4$ ,  $\text{AgNO}_3$ , and  $\text{BaCl}_2$ . The solution would contain the following ions:  $\text{Na}^+$ ,  $\text{Ag}^+$ ,  $\text{Ba}^{++}$ ,  $\text{SO}_4^{--}$ ,  $\text{NO}_3^-$ , and  $\text{Cl}^-$ . These ions could not all exist together in solution;  $\text{BaSO}_4$ ,  $\text{AgCl}$ , and possibly  $\text{Ag}_2\text{SO}_4$  would be precipitated. The rule covering all cases may be stated thus:

If a mixture of salts is soluble in water, only those anions can be present which form soluble salts with all cations present.

*Example 5:* The sample is completely insoluble in water but readily soluble in cold dilute  $\text{HCl}$ ; nickel and zinc are present.

The only possible anions are those which form water-insoluble salts with both nickel and zinc. Furthermore, these insoluble salts must all be soluble in dilute  $\text{HCl}$ .

Nitrates, acetates, chlorides, bromides, iodides, and sulfates are absent (Rules 1, 3 and 4), since they form water-soluble zinc and nickel salts.

Therefore, the following acid radicals may be present: sulfites, sulfides, carbonates, phosphates, and borates. (Chromates and arsenates are absent, since neither chromium nor arsenic were found in the metal analysis.)

*Example 6:* Copper and sodium are present. The sample is partially soluble in water and completely soluble in dilute  $\text{HCl}$ .

When a salt is partially soluble in water no acid radical can be eliminated on the basis of this partial solubility.

Sulfides can be eliminated since  $\text{CuS}$  is not readily soluble in dilute  $\text{HCl}$  (see analysis of copper-arsenic group).

Therefore, the following acid radicals might be present: sulfates, sulfites, carbonates, phosphates, borates, chlorides, bromides, iodides, acetates, and nitrates. (Chromates and arsenates are absent since chromium and arsenic were not found in the regular metal analysis.)

In actual practice, elimination of anions on the basis of insolubility is not always satisfactory and should not be relied upon too much. In the first place, the salt may have been fused or sintered in the course of its commercial preparation, with the result that it dissolves so

slowly that it appears to be practically insoluble. In the second place, a soluble salt may hydrolyze to form an insoluble hydroxide or basic salt, giving the net effect of insolubility.

It is obvious from the examples cited that solubility information alone does not make possible any eliminations; solubility information must be combined with other facts.

## ANALYSIS FOR CATIONS AND ANIONS

### Procedure 47: Analysis for cations

Proceed as follows:

1. Make a list of those cations which can be definitely eliminated on the basis of the solubility of the solid, the color of the solution, and the anion analysis (if the anion analysis has been carried out).
2. Carry out a complete cation analysis for those cations not eliminated in Step 1. Use a solution prepared according to Procedure 46(A) or 46(B).

### NOTES

1. If a solution is prepared in Procedure 46(B) by dissolving the solid in cold HCl, then  $\text{Ag}^+$ ,  $\text{Hg}^+$ , and  $\text{Pb}^{++}$  must be absent, since they would form insoluble chlorides. The cation analysis will then start with Procedure 5.

2. If the salt mixture is soluble in water, blanket tests for certain large groups of cations may be made as follows:

(a) To a few drops of the water solution add  $\text{Na}_2\text{CO}_3$  solution until no longer acidic. If no precipitate forms, all cations except  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ , and  $\text{As}^{+++}$  are absent.  $\text{Na}_3\text{PO}_4$  may be substituted for  $\text{Na}_2\text{CO}_3$  if the solution is not acidic.

(b) To a few drops of the water solution add 8N NaOH until distinctly alkaline and stir for 1 minute. The absence of a precipitate eliminates all cations except  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Ba}^{++}$ ,  $\text{Ca}^{++}$ ,  $\text{Zn}^{++}$ ,  $\text{Cr}^{+++}$ ,  $\text{Al}^{+++}$ ,  $\text{Pb}^{++}$ ,  $\text{Sn}^{++}$ ,  $\text{Sn}^{++++}$ ,  $\text{Sb}^{+++}$ , and  $\text{As}^{+++}$ .

(c) To a few drops of the water solution add 15N  $\text{NH}_4\text{OH}$  until distinctly alkaline and stir for 1 minute. The absence of a precipitate eliminates all cations except  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{NH}_4^+$ ,  $\text{Ag}^+$ ,  $\text{Ba}^{++}$ ,  $\text{Ca}^{++}$ ,  $\text{Cu}^{++}$ ,  $\text{Cd}^{++}$ ,  $\text{Zn}^{++}$ ,  $\text{Ni}^{++}$ ,  $\text{Co}^{++}$ , and  $\text{As}^{+++}$ .

**Procedure 48: Analyses for anions**

Using the solution prepared in Procedure 46(A) or Procedure 46(C) and samples of the solid unknown, make a complete anion analysis in the following order (see Notes 11 and 12, Procedure 46).

1. Make a list of the anions that can be eliminated on the basis of the solubility of the solid, the cation analysis, and the color of the solution.

2. Carry out the three preliminary tests described in Procedures 29, 30, and 31. List the anions definitely eliminated by these tests. List, also, the anions definitely proved present by these tests.

3. Carry out specific tests for those anions not definitely proved to be either absent or present by Step 1 or Step 2.

Summarize the results of the cation and anion analyses on the report blank on page 181.

**Questions**

1. From the following list of soluble salts, select (a) 10 pairs which, when brought together in solution, will not react to form a precipitate. (b) Ten pairs which, when brought together in solution, will form a precipitate. Give the formula of the precipitate in each case and write the ionic equation for its formation:  $\text{Pb}(\text{NO}_3)_2$ ,  $\text{Ag}_2\text{SO}_4$ ,  $\text{MgCrO}_4$ ,  $\text{BaS}$ ,  $\text{FeCl}_3$ ,  $\text{NiI}_2$ ,  $\text{ZnBr}_2$ ,  $\text{Na}_3\text{PO}_4$ ,  $\text{K}_2\text{CO}_3$ ,  $(\text{NH}_4)_3\text{AsO}_4$ ,  $\text{NaBO}_2$ ,  $\text{Al}_2(\text{SO}_4)_3$ ,  $\text{Bi}(\text{NO}_3)_3$ ,  $\text{MnCl}_2$ ,  $(\text{NH}_4)_2\text{SO}_3$ ,  $\text{CaS}$ .

2. Give the formula of an acid whose:

- Barium salt is insoluble in water but whose copper salt is soluble.
- Copper salt is insoluble in water but whose calcium salt is soluble.
- Lead salt is insoluble in water but whose zinc salt is soluble.
- Silver salt is insoluble in water but whose copper salt is soluble.
- Mercury I (mercurous) salt is insoluble in water but whose mercury II (mercuric) salt is soluble.
- Manganese salt is insoluble in water but whose potassium salt is soluble.
- Nickel salt is insoluble in water but whose magnesium salt is soluble.

3. Give the symbol for a metal whose:

- Sulfide is insoluble in water but soluble in dilute  $\text{HCl}$ .
- Sulfide is insoluble in dilute  $\text{HCl}$  but soluble in concentrated  $\text{HCl}$ .

- c. Sulfide is insoluble in dilute HCl but soluble in dilute  $\text{HNO}_3$ .
  - d. Hydroxide is insoluble in water but soluble in NaOH.
  - e. Hydroxide is insoluble in water but soluble in  $\text{NH}_4\text{OH}$ .
  - f. Hydroxide is insoluble in  $\text{NH}_4\text{OH}$  but soluble in KOH.
  - g. Hydroxide is insoluble in NaOH but soluble in  $\text{NH}_4\text{OH}$ .
  - h. Hydroxide is insoluble in water but is soluble in  $\text{NH}_4\text{OH}$  and also in NaOH.
  - i. Hydroxide is amphoteric.
  - j. Oxide is insoluble in  $\text{HNO}_3$  but soluble in HCl.
  - k. Chloride hydrolyzes in water to give an insoluble basic chloride.
  - l. Sulfide is completely decomposed in water.
4. Give the simplest and best solvent that could be used to dissolve each of the following:  $\text{ZnS}$ ,  $\text{MgCrO}_4$ ,  $\text{CuSO}_4$ ,  $\text{PbCO}_3$ ,  $\text{Na}_3\text{AsO}_4$ ,  $\text{HgS}$ ,  $\text{AgCl}$ ,  $\text{BiCl}_3$ ,  $\text{NiSO}_3$ ,  $\text{BaSO}_4$ .
5. An unknown salt or mixture of salts is completely soluble in water and contains carbonate and nitrate as the only anions. What cations may be present?
6. An unknown salt or mixture of salts is completely soluble in water and contains  $\text{Cu}^{++}$ ,  $\text{Ag}^+$ ,  $\text{Na}^+$  as the only cations. What anions may be present?
7. An unknown salt or mixture of salts is completely and readily soluble in cold water. On treating the above solution with dilute HCl, effervescence takes place, a colorless, odorless gas being evolved. What metallic ions may be present?
8. An unknown salt or mixture of salts is completely soluble in cold water. On being treated with dilute HCl, the water solution changes in color from yellow to orange red. What metallic ions may be present?
9. A homogeneous powder which is known to contain only one metallic ion dissolves completely in cold water to give a pale-blue solution which turns a very deep blue when treated with  $\text{NH}_4\text{OH}$ . What acid radicals may be present?
10. The chloride of a metal is soluble in cold water. Its hydroxide is white and is insoluble in water and in  $\text{NH}_4\text{OH}$  but dissolves readily in HCl and in KOH. What is the metal?
11. An unknown salt or salt mixture was readily and completely soluble in cold water. The resulting solution was green in color and was found on analysis to contain  $\text{Ni}^{++}$  and  $\text{Cu}^{++}$  as the only cations. List the anions that can be eliminated on the basis of solubility.
12. An unknown salt or salt mixture was readily and completely soluble in cold water. Separate samples of this water solution showed the following behavior: (a) No precipitate when treated with  $\text{AgNO}_3$  solution. (b) No precipitate when treated with  $\text{HNO}_3$  and  $\text{AgNO}_3$  solution. (c) No precipitate when treated with slight excess of  $\text{NH}_4\text{OH}$  and then with  $\text{BaCl}_2$  solu-

tion. (d) No precipitate when acidified with HCl and then treated with BaCl<sub>2</sub> solution. What anions and what cations are eliminated in each test?

**13.** A salt mixture which was readily and completely soluble in cold water showed the following behavior: (a) One sample of the water solution gave a yellow precipitate when acidified with HNO<sub>3</sub> and treated with ammonium molybdate. (b) Another sample of the water solution gave a dark-brown coloration when treated with a mixture of concentrated H<sub>2</sub>SO<sub>4</sub> and ferrous sulfate. (c) A sample of the solid effervesced when treated with cold concentrated H<sub>2</sub>SO<sub>4</sub>. The evolved gas did not fume in moist air but had a very sharp, penetrating odor. What anions are definitely shown to be present? What cations may be present?

**14.** A solid mixture of salts was known to contain sulfate and bromide as the only anions. (a) The solid dissolved readily and completely in cold water to give a clear transparent solution showing no sign of milkiness or opalescence. (b) When a sample of the water solution prepared in (a) was treated with an excess of NaOH, a clear solution with no precipitate was obtained. (c) When a sample of the water solution prepared in (a) was treated with an excess of NH<sub>4</sub>OH, a clear solution with no precipitate was obtained. What anions are definitely shown to be present? What cations may be present?

**15.** A white solid known to be a mixture of sodium salts showed the following behavior: (a) There was no sign of any reaction whatsoever when a sample of the solid was warmed with concentrated H<sub>2</sub>SO<sub>4</sub>. (b) A water solution of the solid gave a white precipitate when made acid with HCl and then treated with BaCl<sub>2</sub>. (c) A water solution of the solid gave no precipitate when acidified with HNO<sub>3</sub> and then treated with AgNO<sub>3</sub>. (d) A water solution of the solid gave a white precipitate when treated with a few drops of AgNO<sub>3</sub>. What anions are shown to be absent?

**16.** Five different solid, dry, anhydrous sodium salts were treated, independently, with cold concentrated H<sub>2</sub>SO<sub>4</sub>. The results listed below for each salt were obtained:

(a) Effervescence. The evolved gas had a light reddish-brown color and a sharp odor and fumed strongly in moist air.

(b) No effervescence. Color of solid changed from yellow to orange.

(c) Effervescence. The evolved gas was colorless and odorless and did not fume in moist air.

(d) Effervescence. The evolved gas was colorless, had a sharp odor, and fumed strongly in moist air.

(e) Effervescence. The evolved gas was colorless and had a very sharp odor but did not fume in moist air and did not discolor a piece of filter paper that had been moistened with a solution of lead nitrate.

Identify each salt.

**17.** A single salt is known to contain magnesium as the only cation. Effervescence takes place when the solid is treated with cold concentrated H<sub>2</sub>SO<sub>4</sub>, a brown gas being evolved. The HCl group test on the water solu-



tion yields a pale-yellow precipitate. When  $\text{H}_2\text{SO}_4$  and  $\text{FeSO}_4$  are added to the water solution, a brown ring forms at the junction of the two liquids. What is the salt?

18. A white solid is completely soluble in cold water. Its water solution is neutral to litmus. No change takes place when the solid is warmed with concentrated  $\text{H}_2\text{SO}_4$ . There is no change when the water solution is treated with  $\text{H}_2\text{SO}_4$  and  $\text{FeSO}_4$ . Which of the following substances may the solid be:  $\text{KNO}_3$ ,  $\text{AlCl}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{Na}_2\text{SO}_4$ ,  $\text{NaBr}$ ,  $\text{BaSO}_4$ ,  $\text{K}_2\text{CrO}_4$ ,  $\text{KCl}$ ,  $\text{NiS}$ ,  $\text{Cr}_2(\text{SO}_4)_3$ ?

19. An unknown solid containing  $\text{Cu}^{++}$  as the only cation was completely insoluble in water but readily soluble in dilute  $\text{HCl}$ . The solution prepared in Procedure 46(C) gave no precipitate either with  $\text{NH}_4\text{OH}$  and  $\text{BaCl}_2$  or  $\text{HNO}_3$  and  $\text{AgNO}_3$ . For what anions must specific tests be made?

20. The sulfide of a metal is insoluble in water but soluble in dilute  $\text{HCl}$ . Its hydroxide is insoluble in water but soluble in both  $\text{NaOH}$  and  $\text{NH}_4\text{OH}$ . What is the metal?

21. A white solid which is known to be a single salt is completely soluble in cold water. This solution is acid to litmus. When the solid is treated with  $\text{HCl}$  nothing happens, when treated with  $\text{H}_2\text{SO}_4$  effervescence takes place, the solid remaining colorless. On treating the water solution with  $\text{NH}_4\text{OH}$ , a white precipitate is formed which redissolves when more  $\text{NH}_4\text{OH}$  is added. When  $\text{BaCl}_2$  is added to the water solution, nothing happens; but when  $\text{AgNO}_3$  is added, a white precipitate is formed. What is the solid?

22. A pure single salt is white, crystalline, and completely soluble in water. When the water solution is acidified with  $\text{HCl}$  and then treated with  $\text{H}_2\text{S}$  a dark-brown precipitate forms. When  $\text{H}_2\text{SO}_4$  is added to the water solution, a white precipitate is formed. When cold concentrated  $\text{H}_2\text{SO}_4$  is added to the dry salt, nothing happens; when the  $\text{H}_2\text{SO}_4$  is heated, however, a brown gas is given off. What is the salt?

23. A copper salt was found to be completely insoluble in water. The prepared solution (made by boiling some of the solid unknown with  $\text{Na}_2\text{CO}_3$  solution, decanting and boiling the decantate with dilute  $\text{HNO}_3$ ) was made slightly alkaline with  $\text{NH}_4\text{OH}$  and  $\text{BaCl}_2$  added. No precipitate resulted. Name the acid radicals possibly present.

24. An unknown salt or mixture of salts is readily and completely soluble in cold water. On being treated with dilute  $\text{HCl}$ , effervescence takes place, a colorless gas with a very sharp, penetrating odor being evolved. What metallic ions may be present?

25. An unknown salt or mixture of salts is completely soluble in water. The colorless solution gives a red flame test. When the water solution is treated with  $\text{AgNO}_3$ , nothing happens. What anions may be present?

26. An unknown was found to be completely soluble in water. The addition of solutions of  $\text{Na}_2\text{HPO}_4$ ,  $\text{BaCl}_2$ , and  $\text{AgNO}_3$  to separate portions of an

aqueous solution of the unknown failed to yield any precipitate. Name the cations and anions possibly present.

**27.** A silver salt was but slightly soluble in water. Upon heating the dry salt with concentrated  $\text{H}_2\text{SO}_4$ , there was no evidence of any reaction. Name the acid radicals possibly present.

**28.** A white crystalline, homogeneous solid which is known to be a single salt dissolves in cold water to give a water-clear solution which reacts acid to litmus paper. Separate samples of this water solution give the following results when treated separately with the following reagents: (a) excess  $\text{NaOH}$ , no precipitate; (b) excess  $\text{NH}_4\text{OH}$ , no precipitate; (c)  $\text{Na}_2\text{CO}_3$ , white precipitate; (d)  $\text{H}_2\text{S}$ , white precipitate; (e) excess  $\text{NH}_4\text{OH} + \text{BaCl}_2$ , white precipitate; (f)  $\text{HNO}_3 + \text{AgNO}_3$ , no precipitate; (g)  $\text{HCl}$ , no sign of any reaction. What is the salt?

**29.** A yellow solid which is known to be a single salt is completely insoluble in hot water but dissolves in hot dilute  $\text{HCl}$  to give an orange-red solution. When this solution is cooled, a white crystalline precipitate forms. This precipitate redissolves when the solution is heated but does not redissolve when cold water is added. What is the salt?

**30.** A green crystalline substance which is known to be a single salt is completely soluble in cold water. When an excess of  $\text{NH}_4\text{OH}$  is added to the water solution, no precipitate is formed, but a deep-blue solution results. When  $\text{H}_2\text{S}$  is added to a water solution which has been acidified with  $\text{HCl}$ , a black precipitate forms. When  $\text{BaCl}_2$  is added to the water solution, nothing happens. When cold concentrated  $\text{H}_2\text{SO}_4$  is added to the solid, effervescence takes place, a colorless strongly fuming gas with a sharp odor being evolved. What could the single salt be?

**31.** A single salt is found to contain  $\text{Zn}^{++}$  as the only cation. The salt is insoluble in water. No visible reaction takes place in the  $\text{H}_2\text{SO}_4$  treatment, no gas being evolved at either high or low temperatures. No precipitate is obtained in the sulfuric acid group test made on the solution prepared according to Procedure 46(C). What is the salt?

**32.** A solid unknown which is readily soluble in dilute  $\text{HCl}$  but insoluble in water is known to contain  $\text{CrO}_4^{--}$ . How would you determine whether or not it also contained  $\text{Cr}^{+++}$ ?

**33.** A solid unknown which is insoluble in water but soluble in dilute  $\text{HCl}$  is known to contain  $\text{Cr}^{+++}$ . How would you determine whether or not it also contained  $\text{CrO}_4^{--}$ ?

**34.** How distinguish, by means of simple tests, between the following dry salts?

- |   |  |
|---|--|
| a. $\text{BaSO}_4$ and $\text{Pb}(\text{NO}_3)_2$ .   | f. $\text{Bi}_2(\text{CrO}_4)_3$ and $\text{CuSO}_4$ .         |
| b. $\text{KCl}$ and $\text{ZnS}$ .                    | g. $\text{Cr}(\text{NO}_3)_3$ and $\text{Cd}(\text{NO}_3)_2$ . |
| c. $\text{MnSO}_3$ and $\text{Na}_2\text{CO}_3$ .     | h. $\text{CoCl}_2$ and $\text{AlCl}_3$ .                       |
| d. $\text{AgBr}$ and $\text{FeCl}_3$ .                | i. $\text{NiCO}_3$ and $\text{KBr}$ .                          |
| e. $\text{HgCO}_3$ and $(\text{NH}_4)_3\text{PO}_4$ . | j. $\text{BaCl}_2$ and $\text{PbCO}_3$ .                       |

**35.** Using reactions employed in qualitative analysis, how could you form the following in the laboratory?

- a. Metallic bismuth, starting with  $\text{Bi}_2\text{S}_3$ .
- b.  $\text{FeCl}_3$ , starting with  $\text{Fe}_2(\text{SO}_4)_3$ .
- c. Metallic mercury, starting with  $\text{Hg}(\text{NO}_3)_2$ .
- d. Metallic antimony, starting with  $\text{Sb}_2\text{S}_3$ .
- e.  $\text{KMnO}_4$ , starting with  $\text{MnCl}_2$ .
- f.  $\text{CrO}_5$ , starting with  $\text{Cr}(\text{NO}_3)_3$ .
- g.  $\text{ZnS}$ , starting with  $\text{ZnCO}_3$ .
- h.  $\text{Hg}_2\text{Cl}_2$ , starting with  $\text{HgS}$ .
- i.  $\text{Na}_3\text{AlO}_3$ , starting with metallic aluminum.
- j.  $\text{CuCO}_3$ , starting with  $\text{CuSO}_4$ .
- k.  $\text{SnCl}_2$ , starting with  $\text{Sn}_3(\text{PO}_4)_4$ .

## CHAPTER 11

### Recording and Reporting Analyses

THE FORM USED in recording and reporting analyses of salts and salt mixtures is illustrated by the following example. All solids analyzed will be reported in this manner on the pages in this chapter provided for this purpose.

#### REPORT OF THE ANALYSIS OF SAMPLE NO. 10

DATE: \_\_\_\_\_

**I. Physical Examination:** *White, crystalline, heterogeneous.*

**II. Solubility:** *Soluble in cold water. Colorless solution. No gases evolved.*

#### III. Analysis for Cations

(a) Cations eliminated by the color of the solution:  $Cu^{++}$ ,  $Fe^{+++}$ ,  $Co^{++}$ ,  $Ni^{++}$ ,  $Cr^{+++}$ , and  $Mn^{++}$ .  $CrO_4^{--}$  also absent.

(b) Cations eliminated by the anion analysis: *None. Cation analysis performed before anion analysis.*

(c) Cations eliminated by solubility: *None.*

(d) Results of cation analysis:  $Zn^{++}$  and  $Na^{+}$  present. Blanket tests with  $NaOH$  and  $NH_4OH$  (Notes 2b and 2c of Procedure 47) showed absence of all cations except  $Na^{+}$ ,  $K^{+}$ ,  $NH_4^{+}$ ,  $Ba^{++}$ ,  $Ca^{++}$ ,  $Zn^{++}$  and  $As^{+++}$ .

#### IV. Analysis for Anions

Anions eliminated by color of solution:  $CrO_4^{--}$ .

Anions eliminated in cation analysis:  $AsO_4^{--}$ ,  $CrO_4^{--}$ .

Anions eliminated by solubility:  $SO_3^{--}$ ,  $CO_3^{--}$ ,  $PO_4^{--}$ ,  $BO_3^{--}$ ,  $S^{--}$ ,  $CrO_4^{--}$ ,  $AsO_4^{--}$ .

Results of  $H_2SO_4$  treatment: *Effervescence; gas was colorless, had sharp odor and fumed in moist air;  $Cl^{-}$  indicated;  $Br^{-}$  and  $I^{-}$  absent,  $NO_3^{-}$  probably absent.*

Results of  $AgNO_3$  treatment: *White, curdy precipitate, insoluble in  $HNO_3$ .  $Cl^{-}$  present.*

Results of  $BaCl_2$  treatment: *White precipitate, insoluble in  $HCl$ .  $SO_4^{--}$  present.*

Results of specific tests: *Specific tests made for  $NO_3^{-}$  and  $C_2H_3O_2^{-}$ .  $NO_3^{-}$  and  $C_2H_3O_2^{-}$  absent.*

#### V. Summary

Cations present:  $Zn^{++}$ ,  $Na^{+}$

Anions present:  $SO_4^{--}$ ,  $Cl^{-}$

DATE \_\_\_\_\_

**REPORT OF THE ANALYSIS OF SAMPLE NO. \_\_\_\_\_**

**I. Physical Examination:** \_\_\_\_\_

**II. Solubility:** \_\_\_\_\_

**III. Analysis for Cations**

(a) Cations eliminated by the color of the solution: \_\_\_\_\_

(b) Cations eliminated by the anion analysis: \_\_\_\_\_

(c) Cations eliminated by solubility: \_\_\_\_\_

(d) Results of cation analysis: \_\_\_\_\_

**IV. Analysis for Anions**

(a) Anions eliminated by the color of the solution: \_\_\_\_\_

(b) Anions eliminated by cation analysis: \_\_\_\_\_

(c) Anions eliminated by solubility: \_\_\_\_\_

(d) Results of  $\text{H}_2\text{SO}_4$  treatment: \_\_\_\_\_

(e) Results of  $\text{AgNO}_3$  treatment: \_\_\_\_\_

(f) Results of  $\text{BaCl}_2$  treatment: \_\_\_\_\_

(g) Results of specific tests: \_\_\_\_\_

**V. Summary**

Cations present: \_\_\_\_\_

Anions present: \_\_\_\_\_

DATE \_\_\_\_\_

**REPORT OF THE ANALYSIS OF SAMPLE NO. \_\_\_\_\_**

**I. Physical Examination:** \_\_\_\_\_

**II. Solubility:** \_\_\_\_\_

**III. Analysis for Cations**

(a) Cations eliminated by the color of the solution: \_\_\_\_\_

(b) Cations eliminated by the anion analysis: \_\_\_\_\_

(c) Cations eliminated by solubility: \_\_\_\_\_

(d) Results of cation analysis: \_\_\_\_\_

**IV. Analysis for Anions**

(a) Anions eliminated by the color of the solution: \_\_\_\_\_

(b) Anions eliminated by cation analysis: \_\_\_\_\_

(c) Anions eliminated by solubility: \_\_\_\_\_

(d) Results of  $\text{H}_2\text{SO}_4$  treatment: \_\_\_\_\_

(e) Results of  $\text{AgNO}_3$  treatment: \_\_\_\_\_

(f) Results of  $\text{BaCl}_2$  treatment: \_\_\_\_\_

(g) Results of specific tests: \_\_\_\_\_

**V. Summary**

Cations present: \_\_\_\_\_

Anions present: \_\_\_\_\_

DATE \_\_\_\_\_

**REPORT OF THE ANALYSIS OF SAMPLE NO. \_\_\_\_\_**

**I. Physical Examination:** \_\_\_\_\_

\_\_\_\_\_

**II. Solubility:** \_\_\_\_\_

\_\_\_\_\_

**III. Analysis for Cations**

(a) Cations eliminated by the color of the solution: \_\_\_\_\_

\_\_\_\_\_

(b) Cations eliminated by the anion analysis: \_\_\_\_\_

\_\_\_\_\_

(c) Cations eliminated by solubility: \_\_\_\_\_

\_\_\_\_\_

(d) Results of cation analysis: \_\_\_\_\_

\_\_\_\_\_

**IV. Analysis for Anions**

(a) Anions eliminated by the color of the solution: \_\_\_\_\_

(b) Anions eliminated by cation analysis: \_\_\_\_\_

(c) Anions eliminated by solubility: \_\_\_\_\_

\_\_\_\_\_

(d) Results of  $\text{H}_2\text{SO}_4$  treatment: \_\_\_\_\_

\_\_\_\_\_

(e) Results of  $\text{AgNO}_3$  treatment: \_\_\_\_\_

\_\_\_\_\_

(f) Results of  $\text{BaCl}_2$  treatment: \_\_\_\_\_

\_\_\_\_\_

(g) Results of specific tests: \_\_\_\_\_

\_\_\_\_\_

**V. Summary**

Cations present: \_\_\_\_\_

Anions present: \_\_\_\_\_

DATE \_\_\_\_\_

**REPORT OF THE ANALYSIS OF SAMPLE NO. \_\_\_\_\_**

**I. Physical Examination:** \_\_\_\_\_

**II. Solubility:** \_\_\_\_\_

**III. Analysis for Cations**

(a) Cations eliminated by the color of the solution: \_\_\_\_\_

(b) Cations eliminated by the anion analysis: \_\_\_\_\_

(c) Cations eliminated by solubility: \_\_\_\_\_

(d) Results of cation analysis: \_\_\_\_\_

**IV. Analysis for Anions**

(a) Anions eliminated by the color of the solution: \_\_\_\_\_

(b) Anions eliminated by cation analysis: \_\_\_\_\_

(c) Anions eliminated by solubility: \_\_\_\_\_

(d) Results of  $\text{H}_2\text{SO}_4$  treatment: \_\_\_\_\_

(e) Results of  $\text{AgNO}_3$  treatment: \_\_\_\_\_

(f) Results of  $\text{BaCl}_2$  treatment: \_\_\_\_\_

(g) Results of specific tests: \_\_\_\_\_

**V. Summary**

Cations present: \_\_\_\_\_

Anions present: \_\_\_\_\_



DATE \_\_\_\_\_

**REPORT OF THE ANALYSIS OF SAMPLE NO. \_\_\_\_\_**

**I. Physical Examination:** \_\_\_\_\_

**II. Solubility:** \_\_\_\_\_

**III. Analysis for Cations**

(a) Cations eliminated by the color of the solution: \_\_\_\_\_

(b) Cations eliminated by the anion analysis: \_\_\_\_\_

(c) Cations eliminated by solubility: \_\_\_\_\_

(d) Results of cation analysis: \_\_\_\_\_

**IV. Analysis for Anions**

(a) Anions eliminated by the color of the solution: \_\_\_\_\_

(b) Anions eliminated by cation analysis: \_\_\_\_\_

(c) Anions eliminated by solubility: \_\_\_\_\_

(d) Results of  $\text{H}_2\text{SO}_4$  treatment: \_\_\_\_\_

(e) Results of  $\text{AgNO}_3$  treatment: \_\_\_\_\_

(f) Results of  $\text{BaCl}_2$  treatment: \_\_\_\_\_

(g) Results of specific tests: \_\_\_\_\_

**V. Summary**

Cations present: \_\_\_\_\_

Anions present: \_\_\_\_\_

DATE \_\_\_\_\_

**REPORT OF THE ANALYSIS OF SAMPLE NO. \_\_\_\_\_**

**I. Physical Examination:** \_\_\_\_\_

**II. Solubility:** \_\_\_\_\_

**III. Analysis for Cations**

(a) Cations eliminated by the color of the solution: \_\_\_\_\_

(b) Cations eliminated by the anion analysis: \_\_\_\_\_

(c) Cations eliminated by solubility: \_\_\_\_\_

(d) Results of cation analysis: \_\_\_\_\_

**IV. Analysis for Anions**

(a) Anions eliminated by the color of the solution: \_\_\_\_\_

(b) Anions eliminated by cation analysis: \_\_\_\_\_

(c) Anions eliminated by solubility: \_\_\_\_\_

(d) Results of  $\text{H}_2\text{SO}_4$  treatment: \_\_\_\_\_

(e) Results of  $\text{AgNO}_3$  treatment: \_\_\_\_\_

(f) Results of  $\text{BaCl}_2$  treatment: \_\_\_\_\_

(g) Results of specific tests: \_\_\_\_\_

**V. Summary**

Cations present: \_\_\_\_\_

Anions present: \_\_\_\_\_

DATE \_\_\_\_\_

**REPORT OF THE ANALYSIS OF SAMPLE NO. \_\_\_\_\_**

**I. Physical Examination:** \_\_\_\_\_

**II. Solubility:** \_\_\_\_\_

**III. Analysis for Cations**

(a) Cations eliminated by the color of the solution: \_\_\_\_\_

(b) Cations eliminated by the anion analysis: \_\_\_\_\_

(c) Cations eliminated by solubility: \_\_\_\_\_

(d) Results of cation analysis: \_\_\_\_\_

**IV. Analysis for Anions**

(a) Anions eliminated by the color of the solution: \_\_\_\_\_

(b) Anions eliminated by cation analysis: \_\_\_\_\_

(c) Anions eliminated by solubility: \_\_\_\_\_

(d) Results of  $\text{H}_2\text{SO}_4$  treatment: \_\_\_\_\_

(e) Results of  $\text{AgNO}_3$  treatment: \_\_\_\_\_

(f) Results of  $\text{BaCl}_2$  treatment: \_\_\_\_\_

(g) Results of specific tests: \_\_\_\_\_

**V. Summary**

Cations present: \_\_\_\_\_

Anions present: \_\_\_\_\_

DATE \_\_\_\_\_

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**I. Physical Examination:** \_\_\_\_\_

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(b) Cations eliminated by the anion analysis: \_\_\_\_\_

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**IV. Analysis for Anions**

(a) Anions eliminated by the color of the solution: \_\_\_\_\_

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(d) Results of  $\text{H}_2\text{SO}_4$  treatment: \_\_\_\_\_

(e) Results of  $\text{AgNO}_3$  treatment: \_\_\_\_\_

(f) Results of  $\text{BaCl}_2$  treatment: \_\_\_\_\_

(g) Results of specific tests: \_\_\_\_\_

**V. Summary**

Cations present: \_\_\_\_\_

Anions present: \_\_\_\_\_

## APPENDIX

### Reagents Used

All liquid reagents and known solutions should be kept on the shelves in small bottles (about 100 ml.) provided with stoppers fitted with medicine droppers. Solid reagents (except the aluminum, zinc, and tin) should be finely powdered or pulverized and should be kept in 250-cc. wide-mouth bottles provided with one-hole No. 8 rubber stoppers fitted with spatulas for dispensing the solid. The handle of the spatula is thrust through the hole of the stopper in such a way that, when the bottle is stoppered, the metal tip of the spatula will be inside the bottle and partly buried in the powdered solid.

### Acids

*Acetic*, dilute, 5N. Dilute 287 cc. of glacial acetic acid with water to 1 liter.

*Hydrochloric*, special concentrated, sp. gr. 1.18–1.20, 12N.

*Hydrochloric*, concentrated, 6N. Dilute 1 volume of the special concentrated acid (12N) with 1 volume of water.

*Hydrochloric*, dilute, 1.5N. Dilute 1 volume of 12N acid with 7 volumes of water.

*Nitric*, concentrated, sp. gr. 1.42, 16N.

*Nitric*, dilute, 3N. Dilute 100 cc. of 16N acid with water to 533 cc.

*Sulfuric*, concentrated, sp. gr. 1.84, 36N.

*Sulfuric*, dilute, 4N. Add 1 volume of concentrated acid to 8 volumes of water.

### Bases

*Ammonium hydroxide*, concentrated, sp. gr. 0.90, 15N.

*Ammonium hydroxide*, dilute, 5N. Dilute 1 volume of concentrated  $\text{NH}_4\text{OH}$  with 2 volumes of water.

*Barium hydroxide*, saturated solution.

*Sodium hydroxide*, 8N. Dissolve 356 g. of solid  $\text{NaOH}$  in water and dilute to 1 liter.

### Salts

*Ammonium acetate*,  $\text{NH}_4\text{C}_2\text{H}_3\text{O}_2$ , 4N. 308 g. per liter of solution.

*Ammonium carbonate*,  $(\text{NH}_4)_2\text{CO}_3$ , 4N. Dissolve 192 g. of the salt in a mixture of about 500 cc. of cold water and 80 cc. of concentrated  $\text{NH}_4\text{OH}$ , and dilute with water to 1 liter.

*Ammonium chloride*,  $\text{NH}_4\text{Cl}$ , 2N. 102 g. per liter of solution.

*Ammonium molybdate*,  $(\text{NH}_4)_2\text{MoO}_4$ . Dissolve 100 g. of  $\text{MoO}_3$  in a mixture of 270 cc. of distilled water and 145 cc. of concentrated  $\text{NH}_4\text{OH}$ . Add this solution slowly and with constant stirring to a mixture of 1150 cc. of water and 490 cc. of 16N  $\text{HNO}_3$ .

*Ammonium nitrate*,  $\text{NH}_4\text{NO}_3$ , N. 80 g. per liter of solution.

*Ammonium oxalate*,  $(\text{NH}_4)_2\text{C}_2\text{O}_4$ , 0.5N. 31 g. per liter of solution.

*Ammonium polysulfide*,  $(\text{NH}_4)_2\text{S}_2$ . Place 270 cc. of concentrated  $\text{NH}_4\text{OH}$  in a bottle immersed in ice. Pass in  $\text{H}_2\text{S}$  slowly until the cold solution is saturated. (Solution becomes light yellow.) Add 450 cc. of concentrated  $\text{NH}_4\text{OH}$ . Then add 18 g. of flowers of sulfur and shake until dissolved. Add 1080 cc. of water. Stir thoroughly.

### NOTE

Ammonium polysulfide will decompose if allowed to stand in open bottles or in contact with air. After it has been prepared it should be kept in small, well-stoppered bottles. If sulfur begins to deposit it is a sign that the  $(\text{NH}_4)_2\text{S}_2$  is decomposing; any such reagent should be discarded. Each freshly opened bottle of  $(\text{NH}_4)_2\text{S}_2$  should be tested for quality as follows: add 10 drops of the reagent to a small amount of freshly precipitated and washed  $\text{SnS}_2$ , and mix thoroughly. The  $\text{SnS}_2$  should be completely dissolved within 1 minute.

*Ammonium sulfate*,  $(\text{NH}_4)_2\text{SO}_4$ , 2N. 132 g. per liter of solution.

*$\alpha$ -Nitroso- $\beta$ -naphthol*,  $\text{C}_{10}\text{H}_6\text{NOOH}$ . Dissolve 0.8 g. of  $\text{C}_{10}\text{H}_6\text{NOOH}$  in 1000 cc. of glacial acetic acid.

*Barium chloride*,  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ , N. 123 g. per liter of solution.

*Chlorine water*. Saturated solution.

*Dimethyl glyoxime*,  $(\text{CH}_3)_2\text{C}_2(\text{NOH})_2$ . Dissolve 10 g. in 1000 cc. of 95 per cent ethyl alcohol.

*Ferrous sulfate*,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ . 200 g. per liter of solution. Place clean scraps of iron in the solution and acidify with a few cc. of  $\text{H}_2\text{SO}_4$ .

*Hydrogen peroxide*,  $\text{H}_2\text{O}_2$ , 3 per cent solution.

*Lead acetate*,  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 3\text{H}_2\text{O}$ , N. 189.5 g. per liter of solution. Add 10 cc. of 5N acetic acid.

*Magnesium reagent*. Dissolve 1 g. of *o-p*-dihydroxy-monoazo-*p*-nitrobenzene in 1000 cc. of 0.25N  $\text{NaOH}$ .

*Magnesia mixture*. Dissolve 110 g. of  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  and 280 g. of  $\text{NH}_4\text{Cl}$  in 1000 cc. of water. Add 262 cc. of 15N  $\text{NH}_4\text{OH}$  and dilute with water to 2000 cc.

*Mercuric chloride*,  $\text{HgCl}_2$ . Saturated solution.

*Potassium chromate*,  $\text{K}_2\text{CrO}_4$ , N. 97 g. per liter of solution.

*Potassium cyanide*,  $\text{KCN}$ , N. 65.2 g. per liter of solution.

*Potassium ferricyanide*,  $\text{K}_3\text{Fe}(\text{CN})_6$ , N. 110 g. per liter of solution.

*Potassium ferrocyanide*,  $\text{K}_4\text{Fe}(\text{CN})_6$ , N. 106 g. per liter of solution.

*Potassium nitrite*,  $\text{KNO}_2$ , N. 85 g. per liter of solution.

*Potassium thiocyanate*,  $\text{KCNS}$ , N. 97 g. per liter of solution.

*Silver nitrate*,  $\text{AgNO}_3$ , 0.25N. 42.5 g. per liter of solution.

*Silver sulfate*,  $\text{Ag}_2\text{SO}_4$ . Saturated solution.

*Sodium acetate*,  $\text{NaC}_2\text{H}_3\text{O}_2$ , N. 82 g. per liter of solution.

*Sodium carbonate*,  $\text{Na}_2\text{CO}_3$ . Saturated solution.

*Sodium cobaltinitrite*. Dissolve 100 g. of  $\text{NaNO}_2$  in a mixture of 200 ml. of distilled water and 52 ml. of 6M acetic acid, and then add 10 g. of  $\text{Co}(\text{NO}_3)_2(\text{H}_2\text{O})_6$ . Allow to stand for 24 hours, filter, and dilute the solution to 400 ml.

*Disodium phosphate*,  $\text{Na}_2\text{HPO}_4$ . 120 g. per liter of solution.

*Stannous chloride*,  $\text{SnCl}_2$ , 0.5N. Dissolve 113 g. of the salt in 500 cc. of concentrated  $\text{HCl}$  and dilute to 1 liter. Keep in a well-stoppered bottle, containing a few pieces of granulated tin.

*Zinc uranyl acetate*. Dissolve 10 g. of uranyl acetate by warming in 6 ml. of 30 per cent acetic acid, and dilute to 50 ml. Mix 30 g. of zinc acetate in 3 ml. of 30 per cent acetic acid and dilute to 50 ml. The solutions are mixed to give a clear solution. Add a small amount of  $\text{NaCl}$  and let stand 24 hours. Decant the clear solution for use.

## Organic liquids

*Carbon tetrachloride*,  $\text{CCl}_4$ .

*Ether, diethyl*,  $(\text{C}_2\text{H}_5)_2\text{O}$ .

*Alcohol, ethyl*,  $\text{C}_2\text{H}_5\text{OH}$ .

*Alcohol, methyl*,  $\text{CH}_3\text{OH}$ .

## Solids

*Aluminum wire*, 28 gauge, 0.0145 in. diameter, cut to 1-in. lengths.

*Tin*, mossy.

*Zinc*, granulated.

*Potassium persulfate*,  $\text{K}_2\text{S}_2\text{O}_8$ .

*Sodium bismuthate*,  $\text{NaBiO}_3$ .

*Sodium peroxide*,  $\text{Na}_2\text{O}_2$ .

## Known Solutions

The "known" solutions for the four groups are made up as follows:

1. **Silver group.** 10 g. of  $\text{AgNO}_3$ , 50 g. of  $\text{HgNO}_3$ , 50 g. of  $\text{Pb}(\text{NO}_3)_2$ , and 5 cc. of 16N  $\text{HNO}_3$  per liter of water solution. First dissolve the  $\text{HgNO}_3$ , heating the solution. Then dissolve the  $\text{Pb}(\text{NO}_3)_2$  and the  $\text{AgNO}_3$  in order.

2. **Copper-arsenic group.** 15 g. of  $\text{PbCl}_2$ , and 50 g. each of  $\text{HgCl}_2$ ,  $\text{BiCl}_3$ ,  $\text{CdCl}_2$ ,  $\text{CuCl}_2$ ,  $\text{SbCl}_3$ ,  $\text{SnCl}_4$ , and  $\text{Na}_3\text{AsO}_4$  in a solution containing 600 cc. of 12N  $\text{HCl}$  and 400 cc. of water. First dissolve the  $\text{PbCl}_2$ ,

heating to boiling to speed up the rate of solution. Then dissolve the  $\text{Na}_3\text{AsO}_4$ , then the other components in any desired order.

3. **Aluminum-nickel group.** 50 g. each of  $\text{AlCl}_3$ ,  $\text{FeCl}_3$ ,  $\text{CrCl}_3$ ,  $\text{CoCl}_2$ ,  $\text{NiCl}_2$ ,  $\text{MnCl}_2$ , and  $\text{ZnCl}_2$  and 50 cc. of 12N HCl per liter of water solution. The components may be dissolved in any order.

4. **Barium-magnesium group.** 50 g. each of  $\text{MgCl}_2$ ,  $\text{BaCl}_2$ ,  $\text{CaCl}_2$ ,  $\text{KCl}$ ,  $\text{NaCl}$ , and  $\text{NH}_4\text{Cl}$  per liter of water solution. Dissolve in any order.

### Unknown Solutions

The "unknown" solutions should be prepared in the same concentrations as the "known" solutions and the same salts should be used.

### Solids for Experiments 1 and 4

Zinc sulfide, potassium nitrate, borax or sodium metaborate, and the sulfate, sulfite, carbonate, chromate, chloride, bromide, iodide, acetate, phosphate, and arsenate of sodium or potassium.

### Solutions for Experiments 2, 3, and 4

Normal solutions of the sodium, potassium, or ammonium salts of each of the 13 anions ( $\text{C}_2\text{H}_3\text{O}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{S}^{2-}$ ,  $\text{SO}_4^{2-}$ ,  $\text{SO}_3^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{CrO}_4^{2-}$ ,  $\text{BO}_2^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{AsO}_4^{3-}$ ).

### Solutions of Cations

It is desirable to have solutions of each of the cations available.

### List of Equipment Needed

(This equipment can be purchased in standard semimicro size at all laboratory supply houses.)

Beakers, 50, 100, 150 ml.

Beaker cover, aluminum, for 100 ml. beaker, punched to hold  $\frac{3}{8}$ -in. test tubes.

Bottle, 60 ml., wide mouth, with two-hole rubber stopper.

Burner, small, with rubber tubing.

Casserole, 20 ml.,  $1\frac{3}{4}$ -in., porcelain.

Centrifuge, four-tube, to carry  $3 \times \frac{3}{8}$ -in. test tubes. One centrifuge for each three or four students working in a laboratory at one time.

Cork stoppers, tapered, XXXX.

File, three-cornered, small.

Flasks, 125 ml., Erlenmeyer.



Forceps, metal.

Glass tubing, 6 mm.

Graduate, 10 ml.

Hydrogen sulfide bubbling tubes, 5 in.

Hydrogen sulfide generator (central dispensing system or desk-style generators).

Matches.

Medicine droppers and medicine-dropper bulbs.

Ring stand, rings, and clamps.

Spatula, semimicro style, nickel or stainless steel.

Sponge.

Stirring rods,  $5 \times \frac{1}{8}$  in.

Test tubes,  $3 \times \frac{3}{8}$  in.

Test-tube brush, semimicro.

Test-tube holder, wire.

Test-tube rack, wood or metal, for  $\frac{3}{8}$ -in. tubes.

Towels.

Thermometer, 110°C.

Watch glass, 2 in.

Wing top for burner.

Wire gauze, 4 in. square.



# Index

## A

- Acetate, test for, 161
- Acid radicals, elimination of, 134-147, 169, 174
- Acids:
  - group tests for, 135, 141, 145
  - specific tests for, 149-162
- Alloys:
  - analysis of, 125
  - composition of, 126
  - dissolving, 127
- Aluminum, separation and detection of, 99
- Aluminum group, separation from nickel group, 92
- Aluminum-nickel group:
  - analysis of, 87
  - outline of the analysis of, 86
  - precipitation of, 87
- Amalgams, 125
- Ammines, 42
- Ammonium, detection of, 120
- Ammonium polysulfide, properties of, 59, 190
- Amphoteric hydroxides, 67, 92, 93
- Anions:
  - analysis for, 134-162, 174
  - elimination of, 134-147, 169, 174
  - list of, 2
  - specific tests for, 149-162
- Antimony, detection of, 73
- Arsenate, test for, 151
- Arsenic, separation and detection of, 72
- Arsenic group:
  - reprecipitation of, 69
  - separation from copper group, 59

## B

- Barium:
  - precipitation of, 113
  - separation and detection of, 115
- Barium-magnesium group:
  - analysis of, 113
  - outline of the analysis of, 112

- Bismuth, separation and detection of, 66
- Borate, test for, 153
- Bromide, test for, 158

## C

- Cadmium, separation and detection of, 69
- Calcium:
  - detection of, 116
  - precipitation of, 113
- Carbonate, test for, 156
- Cations:
  - analysis for, 2, 164, 173
  - separation into groups, 5
- Chloride, test for, 159
- Chromate, test for, 154
- Chromium, separation and detection of, 101
- Cobalt, detection of, 98
- Colloids, coagulation of, 34
- Common ion, effect on solubility of a precipitate, 31, 89
- Common ion effect, 25, 89
- Copper, separation and detection of, 68
- Copper group, separation from arsenic group, 59

## D

- Dissociation constant, 24

## E

- Equilibrium constant, 21
- Equipment, list of, 192

## F

- Flame test, 115

## I

- Iodide, test for, 158
- Ionic equilibria, 23

Ionization constant, 24  
 Ions, characteristic colors of, 165  
 Iron, separation and detection of, 95

**L**

Laboratory work:  
   record of, 8  
   schedule of, 6  
 Lead:  
   detection of, 41, 64  
   separation and detection of, 40, 64  
   separation of from silver and mercury I, 40

**M**

Magnesium, separation and detection of, 117  
 Magnesium hydroxide, precipitation of, 32, 88  
 Manganese, separation and detection of, 96  
 Mass action, law of, 17  
 Mercury I, separation and detection of, 42  
 Mercury II, separation and detection of, 62

**N**

Nickel, detection of, 98  
 Nickel group, separation from aluminum group, 92  
 Nitrate, test for, 160

**P**

Phosphate, test for, 152  
 Potassium, detection of, 116  
 Precipitates, colloidal, 34  
   occlusion by, 35  
   washing, 35

**Q**

Qualitative analysis:  
   defined, 1  
   practice of, 1

**R**

Reactions, balanced, 20  
   equilibrium, 20

Reagents, list of, 189  
 Record of laboratory work, 8, 180  
 Reference books, 35  
 Reporting analyses, 8, 180

**S**

Salts:  
   complete analysis of, 164  
   physical examination of, 164, 165  
   preparation of solutions of, 166  
   selection of solvent for, 164, 165  
 Silver, separation and detection of, 42  
 Silver group:  
   analysis of, 36  
   equations, 44  
   precipitation of, 37  
 Sodium, detection of, 116  
 Sodium stannite, 67, 68  
 Solubility product, 27  
 Solubility product constant, 28  
 Solubility product principle, application to qualitative analysis, 30  
 Solubility products, table of, 30  
 Solubility rules, 170  
 Solutions, molar, 15  
   known, 6, 191  
   normal, 16  
   percentage, 14  
   saturated, 11  
   supersaturated, 13  
   unknown, 6, 192  
 Sulfate, test for, 155  
 Sulfide, test for, 157  
 Sulfite, test for, 155  
 Sulfuric acid, action on salts, 135

**T**

Thio-salts, 61, 70  
 Tin, detection of, 73

**V**

Velocity constant, 19

**W**

Wash bottle, 39

**Z**

Zinc, separation and detection of, 101















